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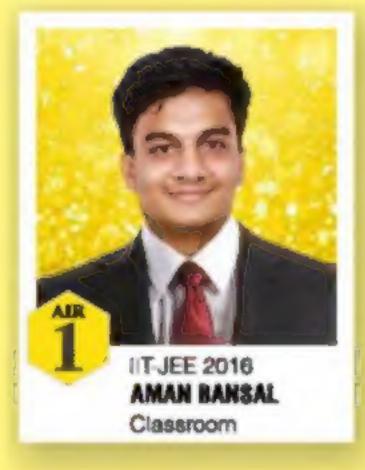
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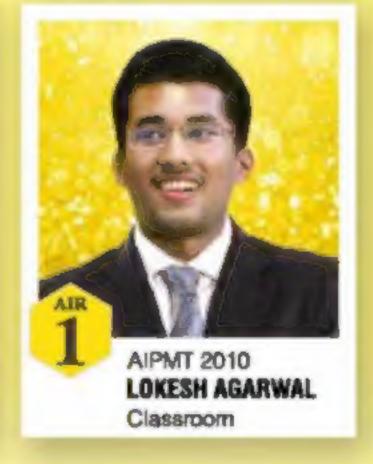












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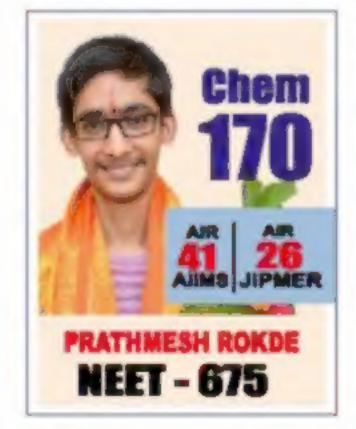


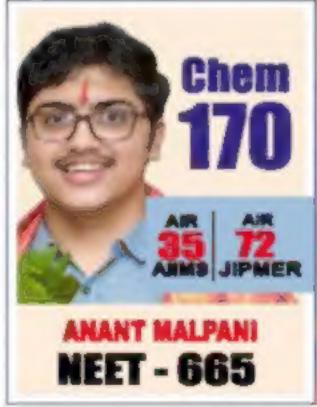
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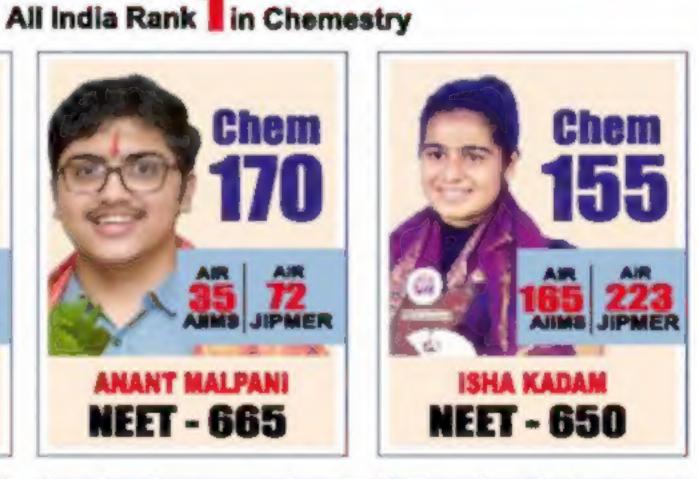


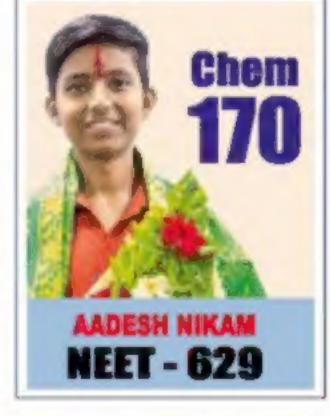
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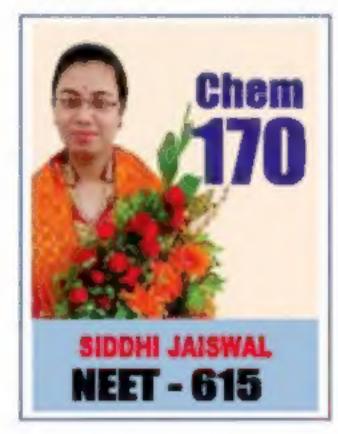


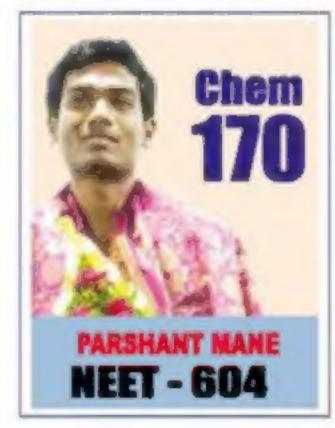




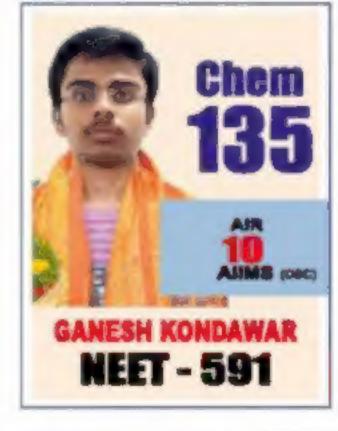


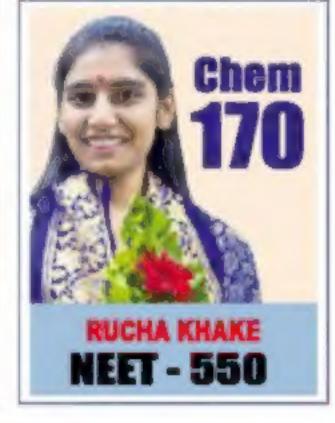












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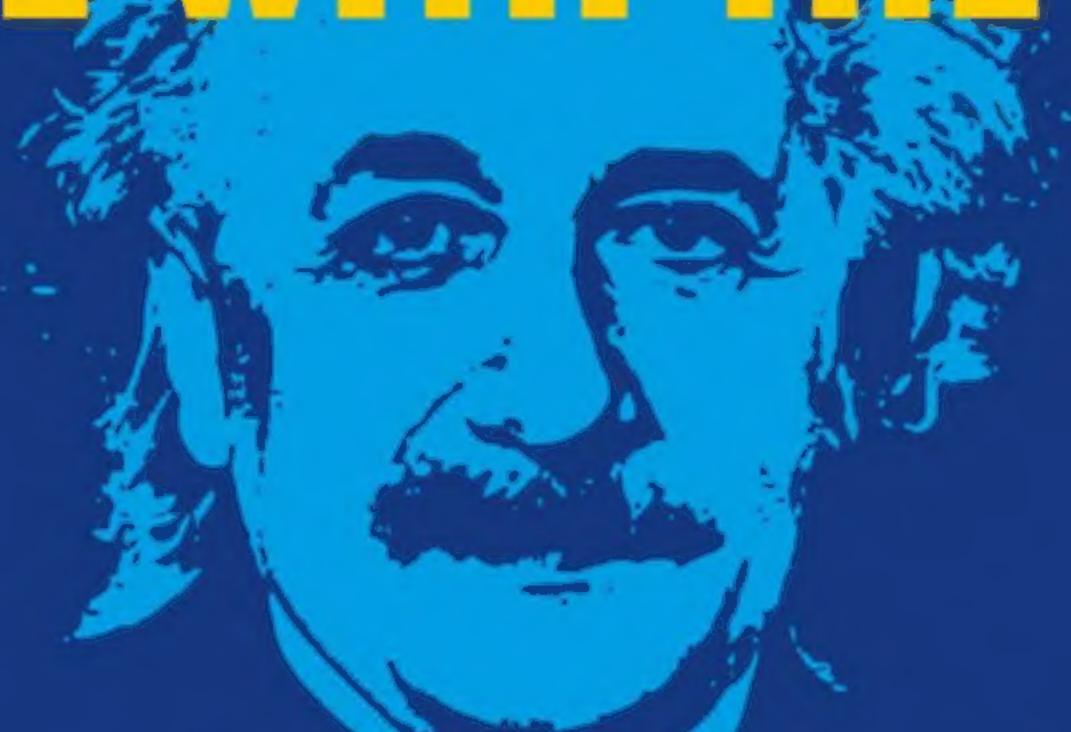
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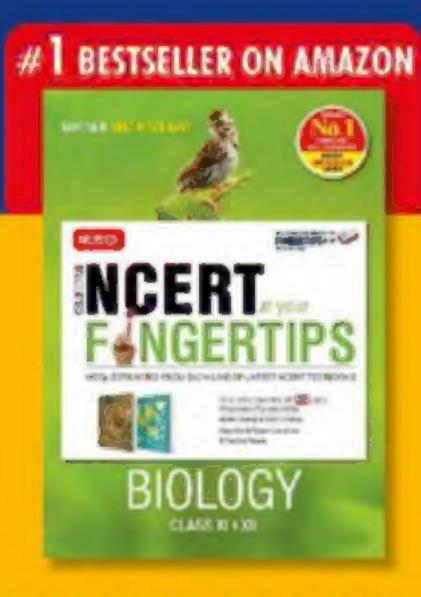
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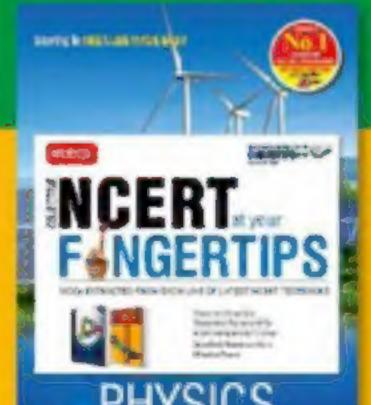
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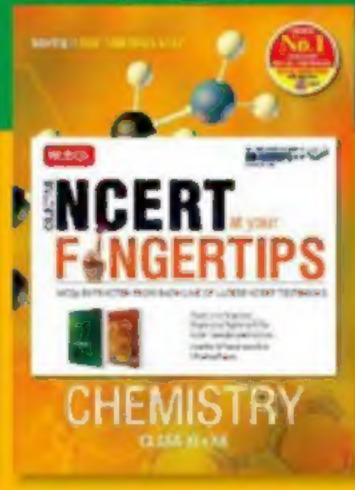


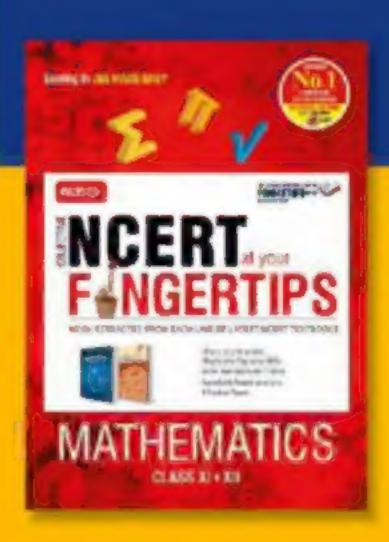
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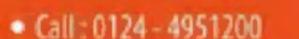
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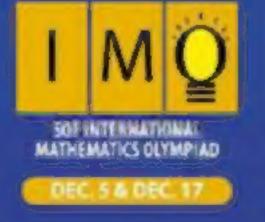
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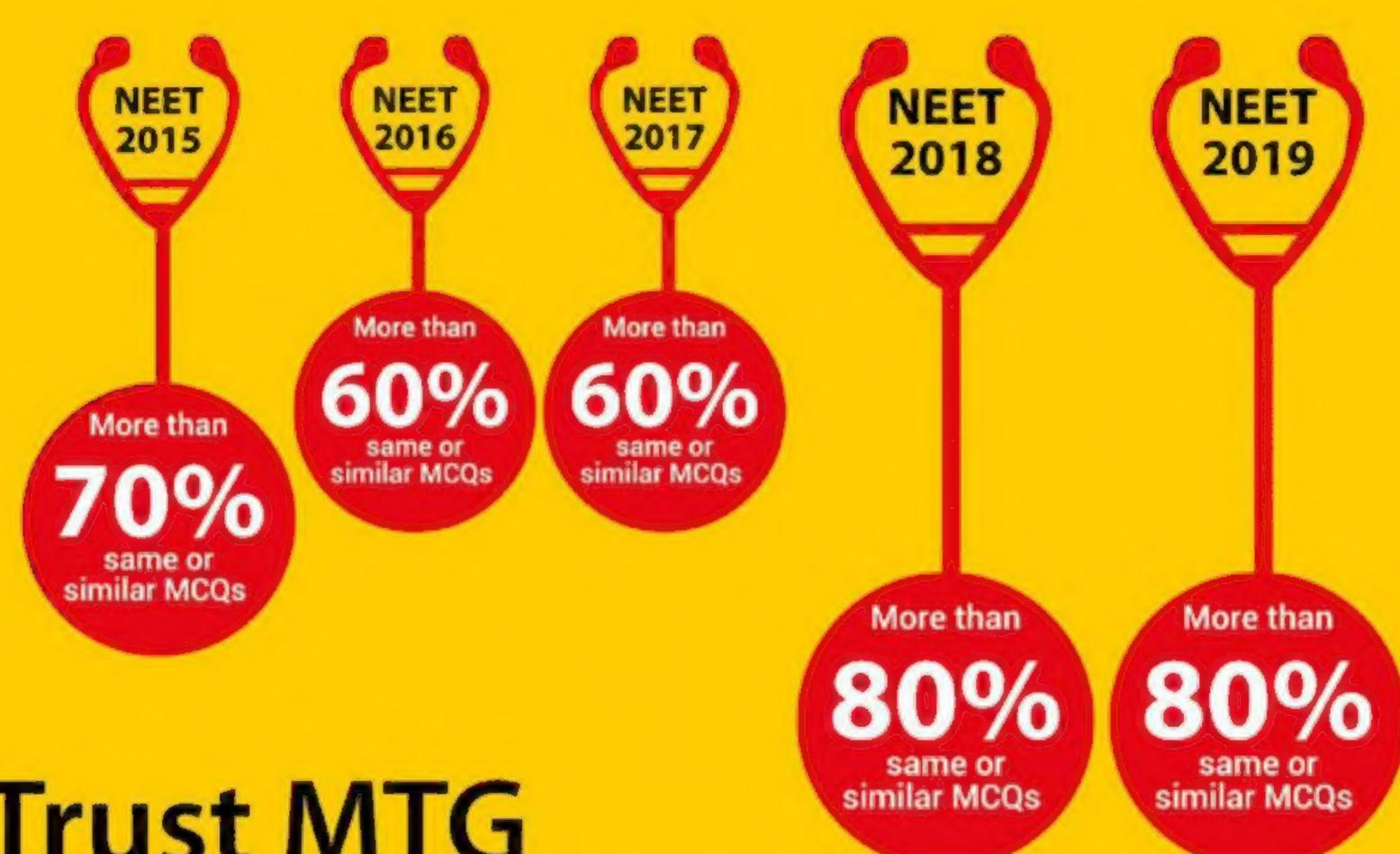








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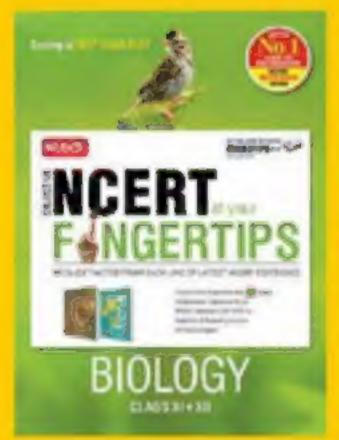


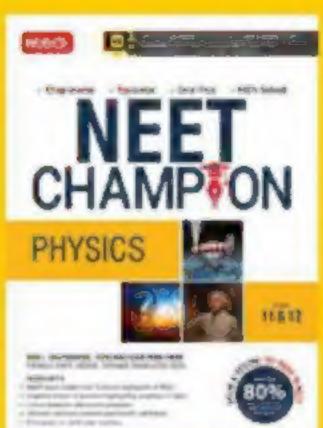
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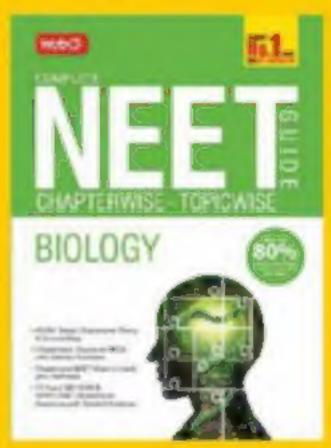
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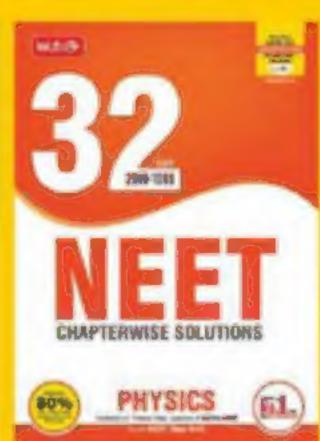
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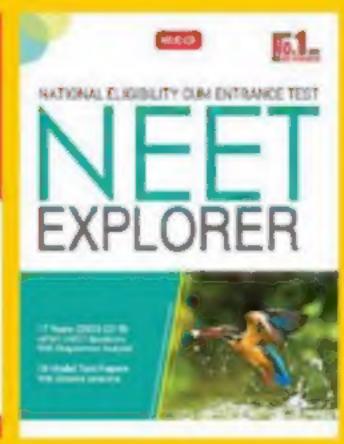
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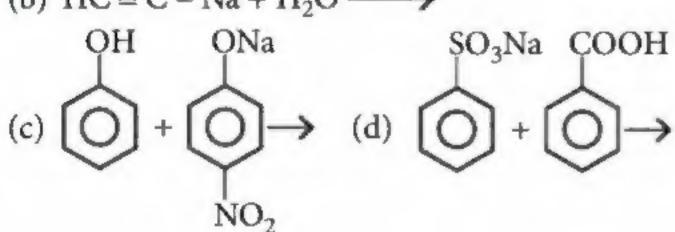
# Exam on May 3, 2020 Class XI

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- 1. Which of the following gives propyne on hydrolysis? (a)  $Al_4C_3$  (b)  $Mg_2C_3$  (c)  $B_4C$  (d)  $La_4C_3$
- The electronegativity of H and Cl are 2.1 and 3.0 respectively. The correct statement about the nature of HCl is
  - (a) 17% ionic
- (b) 83% ionic
- (c) 50% ionic
- (d) 100% ionic.
- For the four gases A, B, C and D, the value of the excluded volume per mole is same. If the order of the critical temperature is  $T_B > T_D > T_A > T_C$ then the order of their liquefaction pressure at a temperature T will be
  - (a)  $P_A < P_B < P_C < P_D$  (b)  $P_R < P_D < P_A < P_C$

  - (c)  $P_C < P_A < P_D < P_B$  (d)  $P_D < P_C < P_A < P_B$
- 4. Which of the following reactions is feasible?
  - (a) CH<sub>3</sub>COOH + HCOONa →
  - (b)  $HC \equiv C Na + H_2O \longrightarrow$



- The wave number of the first line in the Balmer series of hydrogen is 15200 cm<sup>-1</sup>. What would be the wave number of the first line in the Lyman series of the Be<sup>3+</sup> ion?

- (a)  $2.4 \times 10^5 \text{ cm}^{-1}$  (b)  $2.0 \times 10^5 \text{ cm}^{-1}$  (c)  $6.08 \times 10^5 \text{ cm}^{-1}$  (d)  $1.313 \times 10^6 \text{ cm}^{-1}$ (d)  $1.313 \times 10^6 \text{ cm}^{-1}$
- The reaction,  $H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2 O_{(l)}$ , is spontaneous. The  $\Delta S^{\circ} = -163.1 \text{ J mol}^{-1} \text{ K}^{-1}$ . The absolute entropies of  $H_{2(g)}$  and  $O_{2(g)}$  are 130.6 JK<sup>-1</sup> mol<sup>-1</sup> and 205 JK<sup>-1</sup> mol<sup>-1</sup> respectively. What will be the absolute entropy (JK<sup>-1</sup> mol<sup>-1</sup>) of water?
  - (a) 73.2
- (b) 65.6 (c) 70.0

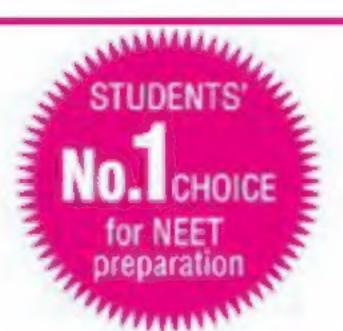
- The predominating product for the following reaction is

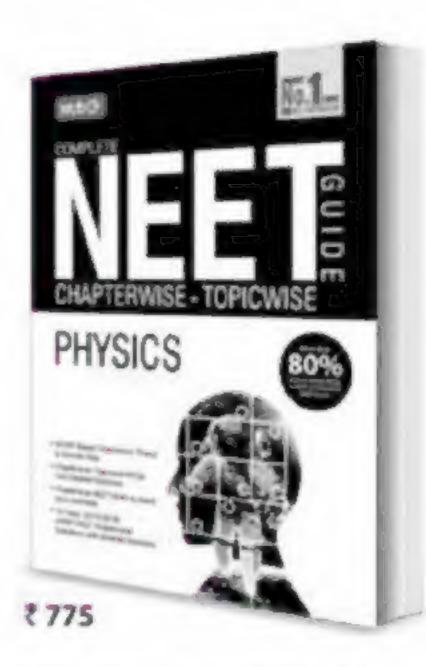
$$CH_2-CH=CH-CH_2\xrightarrow{Zn, CH_3OH} Product$$
Br
Br

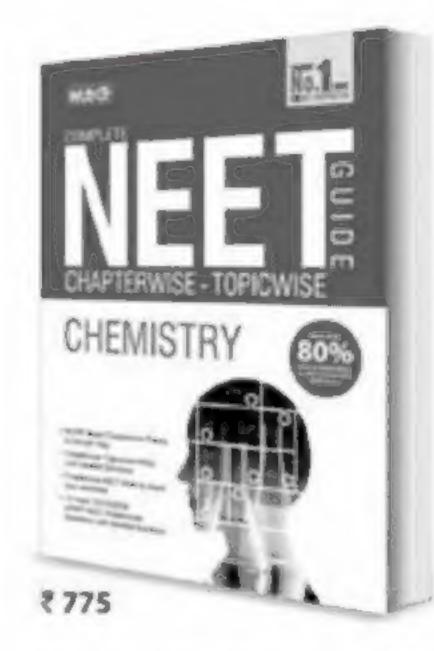
- (a)
- (c)  $CH_2 = CH CH = CH_2$
- (d)

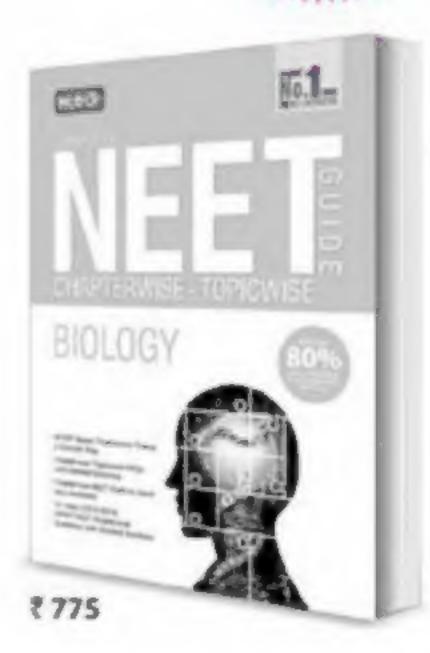
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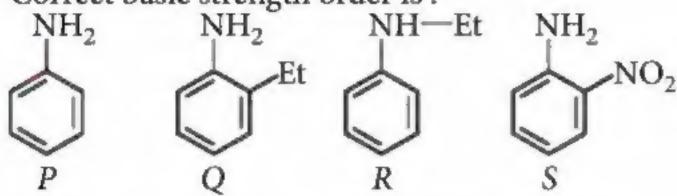


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- What is the atomic number of Livermorium?
  - (a) 106
- (b) 96
- (c) 116
- (d) 118
- Correct basic strength order is:

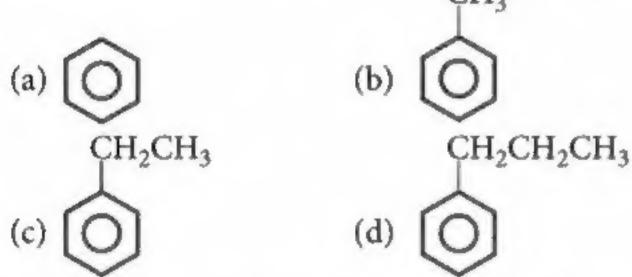


- (a) R > Q > P > S
- (b) R > P > Q > S
- (c) Q > R > P > S
- (d) R > Q > S > P
- 10. When gypsum is totally dehydrated, what is the percentage weight loss?
  - (a) 20.9
- (b) 17.6
- (c) 19.0
- (d) 21.5
- 11. In the following reaction, the product *R* is

$$CaC_2 \xrightarrow{H_2O} P \xrightarrow{\text{Red hot iron tube}} Q \xrightarrow{\text{CH}_3Cl} R$$

$$CH_3$$

$$CH_3$$



- 12. Dissociation constant of a weak acid HA is 10<sup>-7</sup>. 10 mL of aqueous HA of pH value 4 is added with 990 mL of water. Calculate the final pH of acid HA.
  - (a) 5
- (b) 6
- (c) 7
- 13. Number of moles of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> reduced by one mole of Sn<sup>2+</sup> ions is
  - (a) 6
- (b) 3
- (c) 1/6
- (d) 1/3
- 14. An oxide of carbon (X) reacts with ammonia to produce urea, an important fertilizer. Which of the following combinations will not yield (X)?
  - (a)  $CO_3^{2-} + HCl \xrightarrow{\Delta}$  (b)  $CaO + C \xrightarrow{\Delta}$
  - (c)  $C + O_{2(excess)} \xrightarrow{\Delta}$  (d)  $HCO_3^- + HCl \xrightarrow{\Delta}$
- 15. A synthetic mixture of nitrogen and argon has a density of 1.4 gL<sup>-1</sup> at 0 °C and 1 atm pressure. Its average molecular weight and volume percentage of nitrogen in the mixture will be
  - (a) 25.6 and 50
- (b) 31.4 and 72
- (c) 70 and 31.4
- (d) 50 and 25.6

#### SOLUTIONS

- (b):  $Mg_2C_3 + 4H_2O \rightarrow CH_3C \equiv CH + 2Mg(OH)_2$
- (a): % ionic character =  $16(X_A X_B) + 3.5(X_A X_B)^2$  $= 16(3-2.1) + 3.5(3-2.1)^{2} = 16 \times 0.9 + 3.5(0.9)^{2}$ = 14.4 + 2.836 = 17.236 = 17%

3. (b)

- (b)
- (d): Given  $15200 = R(1)^2 \left| \frac{1}{(2)^2} \frac{1}{(3)^2} \right|$

Then 
$$\overline{v} = R(4)^2 \left[ \frac{1}{(1)^2} - \frac{1}{(2)^2} \right]$$
 ...(ii)

From equation (i) and (ii)

$$\bar{\nu} = 1.313 \times 10^6 \, \text{cm}^{-1}$$

(c): Change in standard entropy,

$$\Delta S^{o} = S^{\circ}_{H_2O_{(I)}} - \left[S^{\circ}_{H_2} + \frac{1}{2}S^{\circ}_{O_2}\right]$$

$$-163.1 \text{ J mol}^{-1} \text{ K}^{-1} = S_{\text{H}_2\text{O}(i)}^{\circ} - \left[ 130.6 + \frac{205}{2} \right]$$

Absolute entropy of water =  $70.0 \text{ JK}^{-1} \text{ mol}^{-1}$ .

OCTOBER 2019



Try to find as many as words related organic chemistry. Readers can send their responses at editor@mtg.in or post us with complete address by 10<sup>th</sup> of every month. The name of the reader who will give more than twenty correct answer, will be published in next issue.

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5	Н	Υ	P	E	R	C	0	Ν	J	U	G	Α	T	1	0	N	1	K	L	N	A
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X	1	P	Е	A	D	A	C	0	N	D	Е	N	S	A	T	1	0	N	C	R	P
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C	L	N	1	Q	Α	L	K	Α	N	E	Χ	U	1	T	T	N	0	M	M	5	N
1	K	D	Α	N	В	R	E	5	0	N	Α	N	C	E	Н	М	Н	C	В	F	5
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A	F	Ε	P	Н	D	L	C	0	В	R	5	Α	Q	0	R	D	D	G	S	L	T
N	S	N	0	R	Υ	1	E	J	X	В	1	N	D	T	٧	R	R	1	T	P	U
H	5	P	Q	L	K	D	J	В	1	Y	X	H	W	٧	N	T	0	5	1	Q	R
Υ	T	N	5	1	٧	Q	E	М	0	R	L	Α	D	E	Χ	Υ	Χ	Q	0	P	A
D	X	Z	Α	C	E	R	5	D	Q	N	N	1	P	0	L	N	Υ	1	N	S	T
R	C	E	R	Q	N	1	E	Α	M	1	D	E	C	C	В	E	F	1	Н	G	E
1	Н	N	P	Q	R	T	5	U	Χ	E	N	D	Α	A	L	K	Е	N	E	R	D
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1	A	N	F	0	Χ	-	D	A	T	1	0	N	Q	D	Α	0	Z	Y	Α	Z	C
5	Α	P	0	N	1	F	F.	C	Α	T	1	0	N	P	C	Υ	0	L	C	P	Α

7. (c): 
$$Zn \longrightarrow Zn^{2+} + 2e^{-}$$
 $CH_2CH = CHCH_2S \longrightarrow CH_2 \longrightarrow CH = CH \longrightarrow CH_2 + Br^{-}$ 
 $Br$ 
 $Br$ 
 $CH_2 = CH - CH = CH_2 + ZnBr_2$ 

10. (a): Molecular weight of gypsum,  $CaSO_4 \cdot 2H_2O$ = 172 g

Weight of water of hydration =  $2 \times 18 = 36$  g 172 g loses 36 g of water on dehydration.

Percentage weight loss = 
$$36 \times \frac{100}{172} = 20.9$$

11. (b): Hydrolysis of calcium carbide produces acetylene with calcium hydroxide.

CaC<sub>2</sub> 
$$\xrightarrow{2H_2O}$$
 C<sub>2</sub>H<sub>2</sub> + Ca(OH)<sub>2</sub>

$$(P)$$
3C<sub>2</sub>H<sub>2</sub>  $\xrightarrow{\text{Red hot iron tube}}$   $O$ 

$$(P)$$

$$(Q)$$
Benzene

This is the synthetic method for the preparation of benzene.

$$\begin{array}{c}
CH_3\\
+ CH_3Cl \xrightarrow{\text{Anhy. AlCl}_3}
\end{array}$$

$$\begin{array}{c}
(R)\\
\text{Toluene}
\end{array}$$

This is known as Friedel-Craft's alkylation reaction, which results in production of homologue of arene.

12. (a): Given, pH = 4, [H<sup>+</sup>] = 
$$10^{-4}$$
 M
$$[H^+] = \sqrt{K_a C}, 10^{-4} = \sqrt{10^{-7} C}$$
Initial concentration of the weak acid, HA = C = 0.1 mol L<sup>-1</sup>
Final concentration of the acid HA =  $\frac{10 \times 0.1}{1000}$ 
=  $10^{-3}$  mol L<sup>-1</sup>

$$[H^+] = \sqrt{K_a C} = \sqrt{10^{-7} \times 10^{-3}} = 10^{-5} \text{ M}$$
  
 $pH = -\log 10^{-5} = 5 \log 10 = 5$ 

13. (d): 
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
  
 $Sn^{2+} \longrightarrow Sn^{4+} + 2e^-] \times 3$   
 $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$   
 $+ 7H_2O$ 

Here 3 moles of  $\operatorname{Sn}^{2+}$  ions reduce  $\operatorname{K}_2\operatorname{Cr}_2\operatorname{O}_7=1$  mole  $\therefore$  1 mole of  $\operatorname{Sn}^{2+}$  ions will reduce  $\operatorname{K}_2\operatorname{Cr}_2\operatorname{O}_7=1/3$  mole.

- 14. (b): (X) is CO₂ because CO₂ and NH₃ under pressure gives urea which is used as a fertilizer. Reaction (b) does not produce CO₂ CaO + 3C → CaC₂ + CO
- 15. (b): Molecular weight (M) can be obtained from density (d) as,  $M = \frac{dRT}{P}$ Average molecular weight of the mixture  $= \frac{1.4 \times 0.0821 \times 273}{1} = 31.4$ If the % volume of N<sub>2</sub> is 'x'.  $31.4 = \frac{x \times 28 + (100 x)40}{100}$   $\Rightarrow 12x = 860 \Rightarrow x = 71.6 \approx 72$ Thus, volume percentage of N<sub>2</sub> in the mixture = 72



#### **NEET 2020 DATE SHEET RELEASED**

The entrance exam for the MBBS/BDS courses in India — National Eligibility cum Entrance Test (NEET) for undergraduate courses is going to be held on May 3, 2020 (Sunday). This is the second time the National Testing Agency (NTA) will be conducting the NEET. The application process will begin from December 2 and will close on December 31. Interested candidates can apply at ntaneet.nic.in.

All those candidates who have passed class 12 are eligible to appear for the National Eligibility Entrance Test (NEET UG 2020). The exam will be held in the pen-and-paper mode and from March 27, the applicants can download the NEET admit card. The result for NEET is scheduled to release on June 4.

NEET is a three-hour long exam which includes three sections — physics, chemistry and biology. Of the total 180 questions, 90 would be from biology and 45 each from physics and chemistry. Preparation syllabus includes the whole of class 11 and 12 standard NCERT textbooks in the respective subjects.

Every correct answer would get plus four marks and every incorrect answer result in a negative mark. Questions that are not attempted do not have any penalty marks. The National Testing Agency (NTA) has been set-up by the government of India responsibility of NTA to conduct the entrance test. Competitive entrance exams including NEET UG, JEE, NET, etc. were earlier conducted by CBSE. In NEET 2019, record 15 lakh candidates applied and the exam was held on May 5.



Brush up your concepts to get high rank in NEET/JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-luned to the requirements of these Entrance Tests.

2020



### **Equilibrium** | Redox Reactions



- Equilibrium is the state of reaction which proceeds in both the forward and backward directions at the equal speed or the state of chemical reaction in which concentrations of reactants and products become constant at constant temperature and pressure irrespective of the initial state.
   Equilibrium is of two types:
  - (i) Physical equilibrium (ii) Chemical equilibrium

#### PHYSICAL EQUILIBRIUM

It is the process which involves only, physical changes like equilibrium between different states of substances at a particular temperature.

- Solid ⇌ Liquid: ice ⇌ water at 0°C rate of melting = rate of freezing
- Liquid ⇌ Gas (vapour):

  water (liquid) ⇌ water (vapours) at 100°C

  rate of evaporation = rate of condensation
- Solid ⇌ Gas (vapour):
   CO<sub>2</sub> (solid) ⇌ CO<sub>2</sub> (vapours)
   rate of sublimation = rate of deposition
- Solid 
   ⇒ Saturated solution of solid in liquid:
   rate of dissolution = rate of precipitation
   sugar (solid) 
   ⇒ sugar (in solution)
- Gas 
   ⇒ Saturated solution of gas in liquid; it is always exothermic and spontaneous.
   CO<sub>2</sub> (gas) ⇒ CO<sub>2</sub> (in solution)

#### CHEMICAL EQUILIBRIUM

If the process involves only chemical changes, the equilibrium is called chemical equilibrium.

 Reversible reaction: A reaction in which not only the reactants react to form products but also the reactants are formed back by the reaction of products with each other at the given conditions of the reaction. These reactions if carried out in a closed vessel do not go to completion.

$$e.g.$$
,  $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ 

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

- Irreversible reaction: These are the reactions in which products do not react back to give the reactants, i.e., reaction cannot be retraced at any point. e.g., rusting of iron, etc.
- State of equilibrium: Chemical equilibrium is that state of a reaction at which the rate of forward reaction becomes equal to rate of backward reaction.
- Dynamic nature of equilibrium: In dynamic equilibrium, changes occur but in opposite directions and at constant rate i.e., forward and backward reactions take place even after the equilibrium is attained but at equal speeds.

#### **Types of Chemical Equilibrium**

 Homogeneous equilibrium: In this type of equilibrium reaction, all the reactants and products are present in same phase.

$$e.g.$$
,  $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$   
 $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)}$   
 $+ H_2O_{(l)}$ 

• Heterogeneous equilibrium: In this type of equilibrium reaction, reactants and products are present in two or more than two different phases.

$$e.g.$$
,  $NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$ ;  
 $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$ 

#### Law of Chemical Equilibrium and Equilibrium Constant

For a reversible reaction,  $aA + bB \rightleftharpoons cC + dD$ Rate of forward reaction  $(R_f) \propto [A]^a [B]^b = k_f [A]^a [B]^b$ Rate of backward reaction,  $(R_b) = k_b [C]^c [D]^d$ At equilibrium,  $R_f = R_b$ 

$$\frac{k_f}{k_b} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}; \text{ where, } K_c \text{ is equilibrium constant.}$$

 $K_c$  is specific for a reaction and this equilibrium equation is also known as law of mass action.

 Relation between equilibrium constants for a general reaction and its multiples:

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	$K_c$
$cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_c^{\prime\prime}=(K_c)^n$
$\frac{1}{n}aA + \frac{1}{n}bB \iff \frac{1}{n}cC + \frac{1}{n}dD$	$K_c^{\prime\prime\prime\prime} = \sqrt[p]{K_c}$

• Relation between  $K_p$  and  $K_c$ :

$$K_c = K_p \left(\frac{1}{RT}\right)^{\Delta n_g} \text{ or } K_p = K_c (RT)^{\Delta n_g}$$
If  $\Delta n_g = 0$ ,  $K_p = K_c$ ; If  $\Delta n_g = +\text{ve}$ ,  $K_p > K_c$ 
If  $\Delta n_g = -\text{ve}$ ,  $K_p < K_c$ 

#### **Units of Equilibrium Constant**

- If  $\Delta n = 0$ , both  $K_c$  and  $K_p$  have no units.
- If  $\Delta n > 0$ , unit of  $K_c = (\text{mol L}^{-1})^{\Delta n_g}$ , unit of  $K_p = (\text{atm})^{\Delta n_g}$

- If  $\Delta n < 0$ , unit of  $K_c = (\text{L mol}^{-1})^{\Delta n_g}$ , unit of  $K_p = (\text{atm}^{-1})^{\Delta n_g}$ 

#### **Applications of Equilibrium Constant**

- Predicting the extent of a reaction: The magnitude of equilibrium constant K indicates the extent to which a reaction can go. In other words, it is a measure of the completion of a reversible reaction. Larger the value of K, greater will be the equilibrium concentration of the components on the right hand side of reaction relative to those on the left hand side, i.e., the reaction proceeds to a greater extent.
- Predicting the direction of a reaction: The equilibrium constant helps in predicting the direction in which a reaction can proceed at any stage. By substituting the concentration of substances that exist in a reaction mixture we can calculate the reaction quotient, Q and comparing the value of Q with the equilibrium constant, K, we can predict whether the reaction will proceed towards products or towards reactants.

Case I: If Q < K, the reaction will proceed in the forward direction.

**Case II**: If Q > K, the reaction will proceed in the backward direction.

**Case III :** If Q = K, the reaction mixture is already in equilibrium.

## Relationship between Gibbs Energy and Equilibrium Constant

- At equilibrium,  $\Delta G^{\circ} = -RT \ln K$ ;  $K = e^{-\Delta G^{\circ}/RT}$
- If  $\Delta G^{\circ} < 0$  then K > 1 [Forward reaction is favoured.]
- If  $\Delta G^{\circ} > 0$  then K < 1 [Reversed reaction is favoured.]
- If  $\Delta G^{\circ} = 0$ , then K = 1 [Reaction is in equilibrium.]

#### **Factors Affecting Equilibria**

Le Chatelier's principle: If a system in equilibrium is subjected to change in concentration, pressure or temperature, equilibrium shifts in the direction that tends to undo the change imposed.

- Effect of change in concentration: Increase in concentration of reactants favours forward reaction and increase in concentration of products favours backward reaction.
- Effect of change in temperature: High temperature favours endothermic reactions and low temperature favours exothermic reactions.
- Effect of change in pressure: High pressure favours the direction in which lesser number of moles of the gas are produced and low pressure favours the

direction in which larger number of moles of the gas are produced.

- Effect of inert gas addition: Addition of inert gas at constant volume does not affect the equilibrium and addition of inert gas at constant pressure favours the direction in which larger number of moles of the gas are produced.
- Effect of adding catalyst: The addition of catalyst does not affect the equilibrium.

#### PEEP INTO PREVIOUS YEARS

- 1. 5.1 g NH<sub>4</sub>SH is introduced in 3.0 L evacuated flask at 327 °C. 30% of the solid NH<sub>4</sub>SH decomposed to NH<sub>3</sub> and H<sub>2</sub>S as gases. The  $K_p$  of the reaction at 327 °C is  $(R = 0.082 \text{ L atm mol}^{-1} \text{ K}^{-1}, \text{ Molar mass})$ of  $S = 32 \text{ g mol}^{-1}$ , molar mass of  $N = 14 \text{ g mol}^{-1}$ )
  - (a)  $0.242 \times 10^{-4} \text{ atm}^2$  (b)  $0.242 \text{ atm}^2$
  - (c)  $1 \times 10^{-4}$  atm<sup>2</sup> (d)  $4.9 \times 10^{-3}$  atm<sup>2</sup>

(JEE Main 2019)

- 2. Which one of the following conditions will favour maximum formation of the product in the reaction  $A_{2(g)} + B_{2(g)} \rightleftharpoons X_{2(g)}, \Delta_r H = -X \text{ kJ } ?$ 
  - (a) Low temperature and high pressure
  - (b) Low temperature and low pressure
  - (c) High temperature and high pressure
  - (d) High temperature and low pressure

(NEET 2018)

3. The equilibrium constants of the following are  $N_2 + 3H_2 \rightleftharpoons 2NH_3; K_1$ 

$$N_2 + 3H_2 \rightleftharpoons 2NH_3; K$$
  
 $N_2 + O_2 \rightleftharpoons 2NO; K_2$ 

$$H_0 + \frac{1}{2}O_0 \Longrightarrow H_0O_0 K$$

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O; K_3$$

The equilibrium constant (K) of the reaction :

$$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$$
 will be

- (a)  $K_2K_3^3/K_1$  (b)  $K_2K_3/K_1$  (c)  $K_2^3K_3/K_1$  (d)  $K_1K_3^3/K_2$

(NEET 2017, 2007, 2003)

#### IONIC EQUILIBRIUM

Ionic equilibrium is the equilibrium existing in solution involving ions or reversible reaction that proceeds through ion formation in water. Ionic compound on dissolution in water splits up into ions, this is called ionisation or dissociation. As aqueous solution of ionic compounds have ions of opposite charges, so they are able to conduct electricity.

#### Ostwald's Dilution Law

Consider the given reaction,

Initial concentration Conc. at equilibrium  $C(1-\alpha)$ where, α is degree of dissociation.

$$K_a = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$
; where,  $K_a$  is

called dissociation or ionisation constant. For a weak electrolyte,  $\alpha <<< 1$  and  $1-\alpha \approx 1$ 

 $K_a = C\alpha^2$  or  $\alpha = \sqrt{\frac{K_a}{C}}$  or  $\alpha = \sqrt{K_a V}$ 

where, V is the volume, containing one mole of electrolyte.

#### Concepts of Acids and Bases

- Arrhenius concept:
  - Arrhenius acid furnishes hydrogen ions in aqueous solution, e.g., HCl.
  - Arrhenius base furnishes hydroxyl ions in aqueous solution, e.g., NaOH.
- Brönsted—Lowry concept:
  - Brönsted acid donates a proton, e.g., HCl.
  - Brönsted base accepts a proton, e.g., NH<sub>3</sub>.
- Conjugate acid base pairs: These are a pairs of acids and bases which differ by a proton, e.g.,

Conjugate acid  $\stackrel{-H^+}{\rightleftharpoons}$  Conjugate base

- Relative strengths of conjugate acids or bases depend upon their tendency to donate a proton or to accept a proton.
- Stronger the acid, weaker is its conjugate base and vice-versa, for example,

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$
  
Strong acid Weak base

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$
Weak acid Strong base

- Lewis concept:
  - Lewis acid accepts a pair of electrons, e.g., BF<sub>3</sub>.
  - Lewis base donates a pair of electrons, e.g., NH<sub>3</sub>.
- Relative strength of acids and bases: This is the ratio of strengths of two weak acids. e.g., for acids  $HA_1$  and  $HA_2$ :

$$HA_1 \rightleftharpoons H^{\dagger} + A_1^{-}; K_{a_1} = C_1 \alpha_1^2$$
  
 $HA_2 \rightleftharpoons H^{\dagger} + A_2^{-}; K_{a_2} = C_2 \alpha_2^2$ 

Relative strength = 
$$\frac{[H^{+}] \text{ furnished by } HA_{1}}{[H^{+}] \text{ furnished by } HA_{2}} = \frac{C_{1}\alpha_{1}}{C_{2}\alpha_{2}}$$

$$= \frac{C_1 \sqrt{K_{a_1}/C_1}}{C_2 \sqrt{K_{a_2}/C_2}} = \sqrt{(K_{a_1}C_1)/(K_{a_2}C_2)} \ (\because \alpha = \sqrt{K_a/C})$$

If concentrations of acids are same  $(C_1 = C_2)$  then,

Relative strength = 
$$\sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

 Similarly, the relative strength of two weak bases of equimolar concentration:

Relative strength of bases = 
$$\sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

#### **Ionisation of Acid and Bases**

• HA 
$$\rightleftharpoons$$
 H<sup>+</sup> + A<sup>-</sup>,  $K_a = \frac{[H^+][A^-]}{[HA]}$   
and degree of ionisation,  $\alpha = \sqrt{\frac{K_a}{C}}$ 

• 
$$BOH \rightleftharpoons B^+ + OH^-, K_b = \frac{[B^+][OH^-]}{[BOH]}$$

# and degree of ionisation, $\alpha = \sqrt{\frac{K_b}{C}}$

# Hydrogen Ion Concentration and Ionic Product of Water

$$pH = -\log[H^{+}] = \log \frac{1}{[H^{+}]} \text{ or } [H^{+}] = 10^{-pH}$$

$$pOH = -\log[OH^{-}] = \log \frac{1}{[OH^{-}]} \text{ or } [OH^{-}] = 10^{-pOH}$$

$$K_{\omega} = [H^{+}][OH^{-}]$$

$$K_w = [H^+][OH^-]$$
  
= Ionic product of water =  $10^{-14}$  (mol/L)<sup>2</sup>  
 $pK_w = -\log K_w$ ,  $pK_w = pH + pOH = 14$ 

• Relationship between  $K_a$  and  $K_b$  or  $pK_a$  and  $pK_b$ :  $pK_a = -\log K_a ; pK_b = -\log K_b$   $K_a \times K_b = [H^+][OH^-]$ So,  $K_a \times K_b = K_w$ or  $pK_w = pK_a + pK_b = 14$  (at 298 K)

#### **Hydrolysis of Salts**

• It is defined as the process in which a salt reacts with water given back the acid and the base.

$$B^+A^- + H_2O \longrightarrow HA + BOH$$
  
Salt water Acid Base

S. No.	Salt	Hydrolysis	Resulting solution	Hydrolysis constant $(K_h)$	Degree of hydrolysis (h)	pН
1.	Weak acid and Strong base	Anionic	Alkaline	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2} \left[ pK_w + pK_a + \log C \right]$
2.	Strong acid and Weak base	Cationic	Acidic	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2} \left[ pK_w - pK_b - \log C \right]$
3.	Weak acid and Weak base	Anionic and Cationic both	Neutral (almost)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$pH = \frac{1}{2} \left[ pK_w + pK_a - pK_b \right]$

#### **Buffer Solutions**

 Buffer solution is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for a long time.

• Types of buffer solutions :

Types	pH
Acidic buffers (pH < 7)	(Henderson-Hasselbalch equation)
(Mixture of weak acid + its salt with a strong base) e.g., CH <sub>3</sub> COOH + CH <sub>3</sub> COONa	$pH = pK_a + log \frac{[Salt]}{[Acid]}$ or $pH = pK_a + log \frac{[Conjugate base]}{[Acid]}$
Basic buffers (pH > 7) (Mixture of weak base and its salt with strong acid) e.g., NH <sub>4</sub> OH + NH <sub>4</sub> Cl	$pH = pK_w - \left(pK_b + \log \frac{[Salt]}{[Base]}\right)$
	or pH = p $K_a$ + log $\frac{[Base]}{[Salt]}$ or pOH = p $K_b$ + log $\frac{[Salt]}{[Base]}$

#### **Solubility Product**

 Solubility product of an electrolyte at a specified temperature may be defined as the product of the molar concentrations of its ions in a saturated solution, each concentration raised to the power equal to the number of ion produced on dissociation of one molecule of electrolyte.

Salt type	Relation between $K_{sp}$ and $S$	Examples
AB	$K_{sp} = (S)(S) = S^2$	AlPO <sub>4</sub> , AgCl, AgBr, PbSO <sub>4</sub> , BaSO <sub>4</sub> , ZnS
$AB_2$	$K_{sp} = (S)(2S)^2 = 4S^3$	PbCl <sub>2</sub> , HgCl <sub>2</sub>
$A_2B$	$K_{sp} = (2S)^2(S) = 4S^3$	Ag <sub>2</sub> CrO <sub>4</sub> , Ag <sub>2</sub> C <sub>2</sub> O <sub>4</sub> , Ag <sub>2</sub> SO <sub>4</sub>
$AB_3$	$K_{sp} = (S)(3S)^3 = 27S^4$	Fe(OH) <sub>3</sub> , Al(OH) <sub>3</sub> , Cr(OH) <sub>3</sub>
$A_3B_2$	$K_{sp} = (3S)^3 (2S)^2$ $= 108S^5$	$Ca_3(PO_4)_2$ , $Zn_3(PO_4)_2$

#### PEEP INTO PREVIOUS YEARS

- 4. Consider the following statements,
  - (i) The pH of a mixture containing 400 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> and 400 mL of 0.1 M NaOH will be approximately 1.3.
  - (ii) Ionic product of water is temperature dependent.
  - (iii) A monobasic acid with  $K_a = 10^{-5}$  has a pH = 5. The degree of dissociation of this acid is 50%.
  - (iv) The Le Chatelier's principle is not applicable to common-ion effect.

The correct statements are

- (a) (i) and (ii)
- (b) (ii) and (iii)
- (c) (i), (ii) and (iv)
- (d) (i), (ii) and (iii)

(JEE Main 2019)

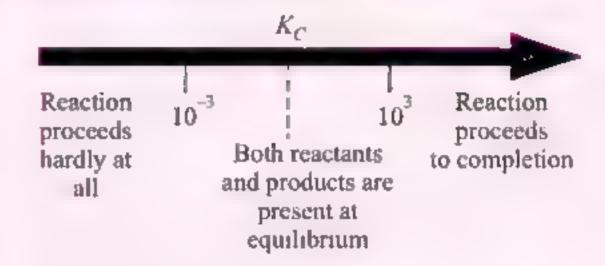
- 5. Which will make basic buffer?
  - (a) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
  - (b) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH<sub>3</sub>COOH
  - (c) 100 mL of 0.1 M CH<sub>3</sub>COOH + 100 mL of 0.1 M NaOH
  - (d) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH<sub>4</sub>OH (NEET 2019)

- 6. The solubility of BaSO<sub>4</sub> in water is  $2.42 \times 10^{-3}$  g L<sup>-1</sup> at 298 K. The value of its solubility product  $(K_{sp})$  will be (Given molar mass of BaSO<sub>4</sub> = 233 g mol<sup>-1</sup>)
  - (a)  $1.08 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$
  - (b)  $1.08 \times 10^{-12} \,\mathrm{mol}^2 \,\mathrm{L}^{-2}$
  - (c)  $1.08 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$
  - (d)  $1.08 \times 10^{-8} \text{ mol}^2 \text{ L}^{-2}$

(NEET 2018)

#### Pourts For Extra Sconnic

Extent of a reaction :



- Larger the value of K<sub>sp</sub>, greater is the solubility of salt in water.
- If  $K_{np} > K_{sp}$ , precipitation occurs.
- Hard acids are those in which acceptor atoms have small size, high electronegativity, low polarisability and possess noble gas configuration.
- Soft acids are those in which acceptor atoms have large size, low electronegativity, high polarisability and do not have noble gas configuration.
- Hard bases have donor atoms with low polarisabilities and high electronegativity.
- Soft bases have donor atoms with high polarisabilities and low electronegativity.
- Greater the value of ionisation constant of the acid or base, smaller is the  $pK_a$  or  $pK_b$  and stronger is the acid or base.
- A decrease in pH by one unit indicates 10 times increase in hydronium ion concentration.
- Indicators are organic substances and are generally weak acids or weak bases.
- An acid-base indicator is an organic dye that detect the end point by a visual change in colour.
- Most indicators do not change colour at a particular pH. They do so over a range of pH from two to three units. This is called pH range which vary for different indicators.

#### Redox Reactions

#### REDOX REACTIONS

When oxidation and reduction reactions take place simultaneously in a reaction then overall process is called redox reaction.

#### Oxidation

There are number of ways to define oxidation:

• It is the process in which electrons are lost from an atom or ion.

$$e.g., \text{Na} \to \text{Na}^+ + e^-; \text{Sn}^{2+} \to \text{Sn}^{4+} + 2e^-$$
  
 $2\text{Cl}^- \to \text{Cl}_2 + 2e^-; \text{Fe}^{2+} \to \text{Fe}^{3+} + e^-$ 

- Oxidation is a process which involves addition of oxygen e.g., C + O<sub>2</sub> → CO<sub>2</sub> (C is oxidised to CO<sub>2</sub>)
   2Mg + O<sub>2</sub> → 2MgO (Mg is oxidised to MgO)
- Removal of hydrogen is also known as oxidation
   e.g., H<sub>2</sub>S + Cl<sub>2</sub> → 2HCl + S (H<sub>2</sub>S is oxidised to S)
- Addition of any eletronegative element is called oxidation e.g., 2Na + Cl<sub>2</sub> → 2NaCl (Na is oxidised)
- Removal of any eletropositive element is termed as oxidation e.g.,

$$2K_2MnO_4 + Cl_2 \rightarrow 2KCl + 2KMnO_4$$
  
(Removal of K oxidation of  $K_2MnO_4$ )

#### Reduction

Reduction is also defined in number of ways:

 It is the process in which an atom or ion gains one or more electrons e.g.,

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$
  
 $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ 

 Reduction is a process which involves removal of oxygen e.g.,

$$CuO + H_2 \rightarrow Cu + H_2O$$
 (CuO is reduced to Cu)

- Addition of hydrogen is also known as reduction e.g., H<sub>2</sub> + Cl<sub>2</sub> → 2HCl (Cl<sub>2</sub> is reduced to HCl)
   Br<sub>2</sub> + H<sub>2</sub>S → 2HBr + S (Br<sub>2</sub> is reduced to HBr)
- Removal of any electronegative element is called reduction e.g.,
   2FeCl<sub>3</sub> + H<sub>2</sub> → 2FeCl<sub>2</sub> + 2HCl (Reduction of FeCl<sub>3</sub>)
- Addition of electropositive element is termed as reduction e.g.,

$$HgCl_2 + Hg \rightarrow Hg_2Cl_2$$
 (Reduction of  $HgCl_2$ )

#### **OXIDATION NUMBER**

 Oxidation number of an element is defined as the charge which an atom of the element has on its ion or in combined state with other atoms.

#### • Some rules for assigning oxidation number :

- The oxidation number of atoms of all the elements in the free state is zero.
- For monatomic ions, the oxidation number of atom is equal to its charge.
- The oxidation number of oxygen in most compounds is -2 except in peroxides (-1), superoxides (-1/2), oxygen difluoride, OF<sub>2</sub> (+2) and dioxygen difluoride, O<sub>2</sub>F<sub>2</sub> (+1).
- The oxidation number of hydrogen is +1,
   except in metal hydrides where it is -1.
- Fluorine always has an oxidation number of −1.
- The algebraic sum of oxidation numbers of all the atoms in a compound must be zero.
- In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion is equal to the net charge on the ion.

#### **Oxidising and Reducing Agents**

- A substance which can gain electrons i.e., undergoing reduction is known as oxidising agent or oxidant.
- A substance which can lose electrons i.e., undergoing oxidation is known as reducing agent or reductant.
- Some important oxidising and reducing agents:

Oxidising agents	Reducing agents	Both reducing and oxidising agents		
KMnO <sub>4</sub> ,	Li, Cs, Na,	H <sub>2</sub> O <sub>2</sub> , SO <sub>2</sub> ,		
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ,	Al, Fe, Zn,	H <sub>2</sub> SO <sub>3</sub> , HNO <sub>2</sub> ,		
NaNO <sub>3</sub> ,	HCl, HBr, HI,	NaNO <sub>2</sub> ,		
CrO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> ,	H <sub>2</sub> S, FeCl <sub>2</sub> ,	Na <sub>2</sub> SO <sub>3</sub> , etc.		
KClO <sub>3</sub> , HNO <sub>3</sub> ,	FeSO <sub>4</sub> , SnCl <sub>2</sub> ,			
SO <sub>3</sub> , FeCl <sub>3</sub> ,	Hg <sub>2</sub> Cl <sub>2</sub> , Cu <sub>2</sub> O,			
O2, O3,	NaH etc.			
P <sub>4</sub> O <sub>10</sub> , etc.				

## Equivalent weights of oxidising and reducing agents

It can be defined as the molecular weight divided by the number of electrons gained or lost respectively as represented in the balanced chemical equation. Equivalent weight of oxidant or reductant

Molecular weight

No. of electrons gained or lost

or Equivalent weight of oxidant or reductant

Formula weight

Total change in oxidation number

#### **Types of Redox Reactions**

- Combination reactions: These are the reactions in which two atoms or molecules combine together to form a third molecule. In these reactions at least one of the reactants must be in elemental form e.g., C+2H<sub>2</sub> → CH<sub>4</sub>
- Decomposition reactions: These are the reactions in which a molecule or compound breaks down to form two or more atoms or molecules. These are simply reverse of combination reactions. For these reactions to be redox reaction one of the products must be in elemental form e.g., 2KClO<sub>3</sub> → 2KCl + 3O<sub>2</sub>
- Displacement reactions: These are the reactions in which an atom or ion in a compound is replaced by another atom or ion. These reactions are represented as

$$AB + C \rightarrow AC + B$$

Displacement reactions are further divided into two categories:

 Metal displacement reactions: If a metal atom/ ion is displaced by another metal atom/ion in the reaction, it is called metal displacement reaction e.g.,

$$TiCl_4 + 2Mg \rightarrow Ti + 2MgCl_2$$

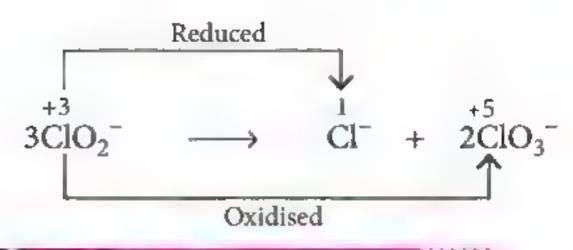
$$CuSO_4 + Zn \rightarrow Cu + ZnSO_4$$

Non-metal displacement reactions: If a non-metal atom/ion is displaced by a metal atom/ion in the reaction, the reaction is called non-metal displacement reaction e.g.,

$$Z_{n}^{0} + H_{2}SO_{4} \rightarrow Z_{n}SO_{4} + H_{2}$$

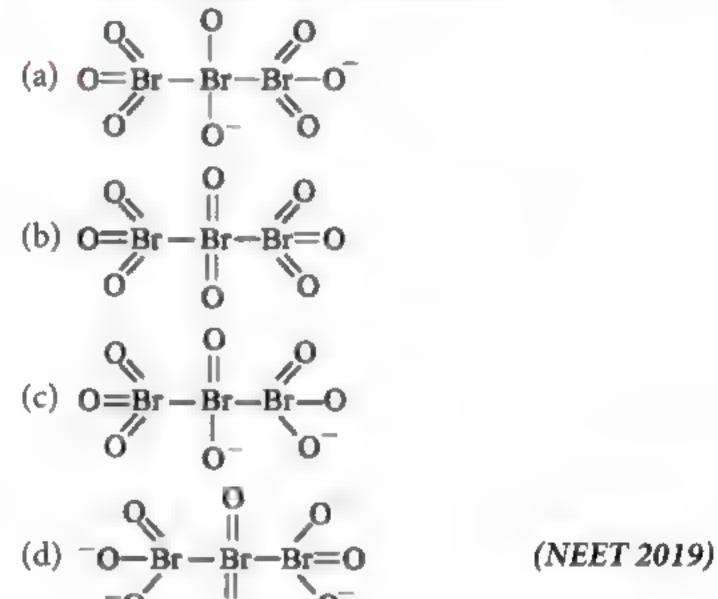
$$_{2Al+3H_{2}O \rightarrow Al_{2}O_{3}+3H_{2}}^{0}$$

 Disproportionation reactions: These are the reactions in which a single species is oxidised as well as reduced simultaneously. In these reactions, the reacting species must have an element which can have at least three variable oxidation states.



#### PEEP INTO PREVIOUS YEARS

- 7. An example of a disproportionation reaction is
  - (a)  $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
  - (b)  $2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$
  - (c)  $2CuBr \rightarrow CuBr_2 + Cu$
  - (d)  $2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$ (JEE Main 2019)
- 8. The correct structure of tribromooctaoxide is



- 9. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?
  - (a)  $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$
  - (b)  $S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$
  - (c)  $C + 2H_2SO_4 \Rightarrow CO_2 + 2SO_2 + 2H_2O$
  - (d)  $CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

(NEET-II 2016)

#### **Balancing of Redox Reactions**

Redox reactions can be balanced by two methods:

- Oxidation number method: This method involves the following steps:
  - Step 1: Write the skeleton redox reaction.
  - **Step 2 :** Identify elements undergoing oxidation or reduction and write the oxidation number of atoms above the symbol.
  - Step 3: Balance, increase in oxidation number and decrease in oxidation number by multiplying the oxidant and reductant with suitable integers.

Step 4: Balance the atoms other than hydrogen and oxygen.

Step 5: Balance hydrogen and oxygen.

- Acidic medium: Add H<sub>2</sub>O to balance O and then add H<sup>+</sup> to balance H atoms.
- Basic medium: Add OH<sup>-</sup> to balance charge and then add H<sub>2</sub>O to balance H and O atoms to the other side.
- Half reaction method: This method involves the following steps:
  - Step 1: Write down the equation in ionic form.
  - **Step 2:** Split the reaction into two half reactions; one for oxidation and other for reduction.
  - **Step 3:** Balance each half reaction by using the following rules:
  - First balance the atoms which undergo oxidation or reduction.
  - Balance the atoms other than hydrogen and oxygen using simple multiples.
  - In acidic and neutral solution: Add water molecules to the side deficient in oxygen and H<sup>+</sup> to the side deficient in hydrogen.
  - In basic medium: For each excess of oxygen add H<sub>2</sub>O to the same side and two OH<sup>-</sup> ions to the other side. If hydrogen is still unbalanced, add one OH<sup>-</sup> ion for each excess of hydrogen on same side and one water molecule to the other side.
  - Step 4: Add electrons to the side deficient in electrons to balance charge.
  - Step 5: Multiply two half reactions by suitable integer to equalise number of electrons in both reactions.
  - **Step 6**: Add the two half reaction to achieve the overall reaction and cancel the electrons on each side.

#### **Redox Titrations**

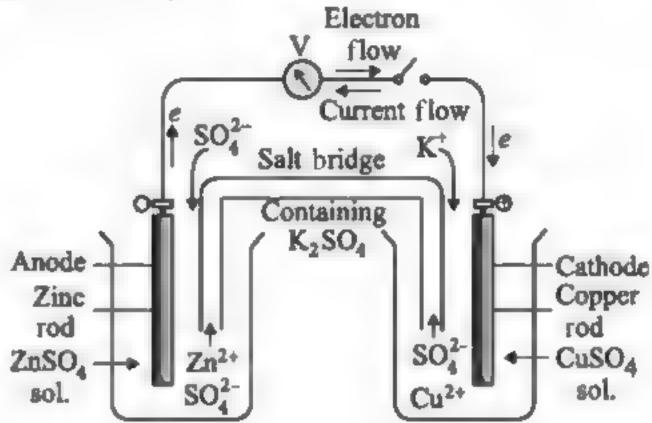
The method is used to determine the strength of a reductant/oxidant using a redox sensitive indicators.

- If the reagent itself is intensely coloured e.g., MnO<sub>4</sub>,
   it can act as self-indicator.
- If there is no auto-colour change, there are indicators which are oxidised immediately after the last drop of the reactant has reacted, producing a dramatic colour change e.g.,  $Cr_2O_7^{2-}$  oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

 Starch is used as indicator in case of those reagents which can either oxidise I ions such as Cu<sup>2+</sup> or reduce I<sub>2</sub> such as S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ions as it gives intense blue colour with molecular iodine.

#### REDOX REACTIONS AND ELECTRODE PROCESSES

 Redox couple: It is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half-reaction. For example, a redox couple is represented as Zn<sup>2+</sup>/Zn and Cu<sup>2+</sup>/Cu;



- Salt bridge: It completes the circuit and used to maintain electrical neutrality.
- Electrode potential: The potential difference set up between the metal and its own ions in the solution is called electrode potential. In general, it is the tendency of an electrode to gain or lose electrons.
- Standard electrode potential (E°): If the concentration of each species taking part in the electrode reaction is unity and the reaction is carried out at 298 K, then the potential of each electrode is called standard electrode potential.
  - Standard electrode potential of hydrogen is taken as 0.00 volts by convention.
  - Electrochemical series: It is a series in which a list of oxidising agents are arranged in decreasing order of their strength. It is also called activity or electromotive series.
  - A negative E° means that the redox couple is a stronger reducing agent than the H<sup>+</sup>/H<sub>2</sub> couple.
  - A positive E° means that the redox couple is a weaker reducing agent than the H<sup>†</sup>/H<sub>2</sub> couple.

#### **Redox Reactions in Everyday Life**

Energy required for daily needs obtained from fuel oxidation.

In extraction of metal, metals are obtained by using suitable reducing agent e.g., coke is used in blast furnace for obtaining iron from Fe<sub>2</sub>O<sub>3</sub> as,

 $Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)}$ 

A breathalyzer test for alcohol makes use of the oxidation of alcohol by dichromate ion which is a redox reaction. The dichromate ion is orange but its reduction product is green Cr3+ ion. The breath of a person who has drunk, contains alcohol vapour, which passess through an acidic solution containing Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, when the person blows through the breathalyzer device, any alcohol in the exhaled air is oxidised, which is signaled by the appearance of green Cr3+. The more alcohol the person has consumed, the greater the intensity of the green colour.

#### PEEP LATE PREVIOUS YEARS

10. Consider the following reduction processes:

$$Zn^{2+} + 2e^{-} \rightarrow Zn_{(s)}$$
;  $E^{\circ} = -0.76 \text{ V}$   
 $Ca^{2+} + 2e^{-} \rightarrow Ca_{(s)}$ ;  $E^{\circ} = -2.87 \text{ V}$   
 $Mg^{2+} + 2e^{-} \rightarrow Mg_{(s)}$ ;  $E^{\circ} = -2.36 \text{ V}$   
 $Ni^{2+} + 2e^{-} \rightarrow Ni_{(s)}$ ;  $E^{\circ} = -0.25 \text{ V}$ 

#### PORTS FOR EXTRA SCORING

- Metals generally exhibit positive oxidation states whereas the oxidation state in case of non-metals may be positive or negative. Moreover, transition elements exhibit variable oxidation states.
- The reverse of disproportionation reaction is called comproportionation reaction in which two reactants each having the same element but in different oxidation states will form a product in which the oxidation state of its both the atoms is similar, e.g., reaction occurring in lead storage battery.

$$Pb_{(s)}^{0} + PbO_{2(s)} + 2H_{2}SO_{4(aq)} \longrightarrow$$

$$2PbSO_{4(s)} + 2H_{2}O_{(l)}$$

The reducing power of the metals increases in the order

- (a) Ca < Zn < Mg < Ni (b) Ca < Mg < Zn < Ni
- (c) Zn < Mg < Ni < Ca (d) Ni < Zn < Mg < Ca(JEE Main 2019)
- 11. The standard (reduction) electrode potentials for metal-metal ion  $(M/M^{2+})$  electrodes P, Q, R and S are respectively -0.44 V, +0.34 V, -0.76 V and - 0.25 V. The increasing order of their reducing capacities is

  - (a) P < R < S < Q (b) Q < S < P < R
  - (c) Q < S < R < P (d) P < R < Q < S

(J & K CET 2019)

12. For the redox reaction,  $MnO_4^- + C_2O_4^{2-} + H^+ \rightarrow Mn^{2+} + CO_2 + H_2O$ 

The correct coefficients of the reactants for the balanced equation are

	$\mathbf{H}^{\star}$	$C_2O_4^{2-}$	$MnO_4^-$	
	2	5	16	(a)
	16	5	2	(b)
	5	16	2	(c)
(NEET 2018)	2	16	5	(d)

- The salt bridge contains only those electrolytes for which the ionic mobilities of cations and anions are nearly the same.
- Lower the electrode potential, stronger is the reducing agent.
- Higher the electrode potential, stronger is the oxidising agent.
- For a disproportionation reaction, equivalent mass of oxidant/reductant = sum of equivalent mass of two half-reactions.

e.g. 
$$4H_3 PO_3 \rightarrow 3H_3 PO_4 + PH_3$$

Eq. mass of H<sub>3</sub>PO<sub>3</sub> = 
$$\frac{M}{2} + \frac{M}{6} = \frac{2M}{3}$$

#### **Answer Key For Peep Into Previous Years**

- (a)
- **(d)**
- (d)

- (c)
- **(b)**
- (d)
- (d)
- **(b)**
- 12.
- (b)

(a)



1. Consider the following reactions in which all the reactants and the products are in gaseous state.

$$2PQ \rightleftharpoons P_2 + Q_2 ; K_1 = 2.5 \times 10^5$$

$$PQ + \frac{1}{2}R_2 \implies PQR \; ; \; K_2 = 5 \times 10^{-3}$$

The value of  $K_3$  for the equilibrium,

$$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \implies PQR$$
, is

- (a)  $2.5 \times 10^{-3}$  (b)  $2.5 \times 10^{3}$
- (c)  $1.0 \times 10^{-5}$  (d)  $5 \times 10^{3}$
- 2. For the reaction,  $X_{(g)} + Y_{(g)} \rightleftharpoons 3Z_{(g)}$  at 25°C, a 3 litre vessel contains 1, 2 and 4 moles of X, Yand Z respectively. Identify the correct statement.
  - (a) The reaction will occur in forward direction if  $K_c$  for the reaction is 10.
  - (b) The reaction will occur in backward direction if  $K_c$  for the reaction is 15.
  - (c) The reaction will be at equilibrium if  $K_c$  for the reaction is 10.66.
  - (d) All of the above.
- 3. 5 g mixture of  $FeSO_4 \cdot 7H_2O$  and  $Fe_2(SO_4)_3 \cdot 9H_2O$ is completely oxidised by 5.5 mL of 0.1 M KMnO<sub>4</sub> in acidic medium. The percentage of FeSO<sub>4</sub>·7H<sub>2</sub>O in mixture is
  - (a) 15.29
- (b) 30.58 (c) 20.24
- (d) 25.29
- 4. How much volume of 0.3 M NH<sub>4</sub>OH should be added to 30 mL of 0.2 M solution of NH<sub>4</sub>Cl to obtain a buffer solution of pH 10.
  - [Given,  $pK_b$  for  $NH_4OH = 4.75$ ]
  - (a) 130.7 mL
- (b) 225 mL
- (c) 112.5 mL
- (d) 109.5 mL
- 5. The correct sequence of the oxidation state of underlined elements is
  - $NaBH_4$ ,  $K_2TaF_7$ ,  $Mg_2P_2O_7$ ,  $Na_2S_4O_6$ ,  $N_3H_1$
  - (a)  $+3, +5, +5, +2.5, -\frac{1}{3}$  (b)  $+5, +3, +5, +3, +\frac{1}{3}$
  - (c) +3, +3, +5, +5,  $-\frac{1}{3}$  (d) +5, +5, +3, +2.5,  $+\frac{1}{3}$
- 6. What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N hydrochloric acid assuming

- complete ionization of the acid and base?
- (a) 12.301 (b) 2.699 (c) 10.546 (d) 11.477

- 7. What is the % dissociation of  $H_2S$ , if 1 mole of  $H_2S$ is introduced in one litre vessel at 1000 K? K for the reaction,
  - $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)} \text{ is } 1 \times 10^{-6}.$
- - (a) 1.67% (b) 1.3% (c) 1.58% (d) 0.01%
- 8. In the disproportionation reaction,  $3HClO_3 \longrightarrow HClO_4 + Cl_2 + 2O_2 + H_2O_3$ , the equivalent mass of the oxidizing agent is (Molar mass of  $HClO_3 = 84.45$ )
  - (a) 16.89 (b) 32.22 (c) 84.45 (d) 28.15

- An element A in a compound ABD has oxidation number  $A^{n-}$ . It is oxidised by  $Cr_2O_7^{2-}$  in acidic medium. In the experiment  $1.68 \times 10^{-3}$  mole of  $K_2Cr_2O_7$  were used for  $3.26 \times 10^{-3}$  mole of ABD. The new oxidation number of A after oxidation is (b) 3-n (c) n-3 (d) +n. (a) 3
- 10. For the following reaction,
  - $CH_3COCH_{3(g)} \rightleftharpoons CH_3CH_{3(g)} + CO_{(g)}$ ; when 1 mole of  $CH_3COCH_{3(g)}$  is taken, initial pressure of CH<sub>3</sub>COCH<sub>3</sub> is 100 mm of Hg. When equilibrium is set up, mole fraction of  $CO_{(g)}$  is 1/3, hence  $K_p$  is
  - (a) 100 mm Hg
- (b) 50 mm Hg
- (c) 25 mm Hg
- (d) 150 mm Hg.
- 11. The degree of dissociation of PCl<sub>5</sub> at a certain temperature and under atmospheric pressure is 0.2. Calculate the pressure at which it will be half dissociated at the same temperature.
  - (a) 2 atm
- (b) 0.225 atm
- (c) 0.12 atm
- (d) 2.50 atm
- 12. The oxidation states of sulphur in Caro's and Marshall's acid are
  - (a) +6, +6 (b) +4, +6 (c) +6, -6 (d) +6, +4

- 13. In which of the following reactions,  $H_2O_2$  acts as a reducing agent?
  - (i)  $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$
  - (ii)  $H_2O_2 2e^- \longrightarrow O_2 + 2H^+$
  - (iii)  $H_2O_2 + 2e^- \longrightarrow 2OH^-$
  - (iv)  $H_2O_2 + 2OH^2 2e \longrightarrow O_2 + 2H_2O$
  - (a) (ii), (iv) (b) (i), (ii) (c) (iii), (iv) (d) (i), (iii)

14. In a saturated solution of the sparingly soluble strong electrolyte AgIO<sub>3</sub> (M.wt. = 283 g/mol), the equilibrium which sets in is

 $AgIO_{3(s)} \rightleftharpoons Ag^{+}_{(aq)} + IO^{-}_{3(aq)}$ 

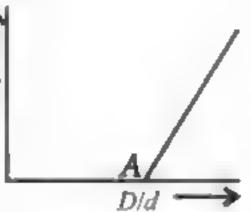
If the solubility product constant  $K_{sp}$  of AgIO<sub>3</sub> at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of AgIO<sub>3</sub> contained in 100 mL of its saturated solution?

- (a)  $1.0 \times 10^{-4}$  g (b)  $28.3 \times 10^{-2}$  g
- (c)  $2.83 \times 10^{-3}$  g (d)  $1.0 \times 10^{-7}$  g
- 15. 3.92 g of ferrous ammonium sulphate are dissolved in 100 mL water. 20 mL of this solution requires 18 mL of potassium permanganate during titration for complete oxidation. The weight of KMnO<sub>4</sub> present in one litre of the solution is
  - (a) 34.76 g (b) 12.38 g (c) 1.238 g (d) 3.51 g
- 16. At a certain temperature, the equilibrium constant  $K_c$  is 16 for the reaction,

$$SO_{2(g)} + NO_{2(g)} \Longrightarrow SO_{3(g)} + NO_{(g)}$$

If 1.0 mol each of all the four gases is taken in a one litre container then the concentration of NO<sub>2</sub> at equilibrium would be

- (a)  $1.6 \text{ mol } L^{-1}$
- (b)  $0.8 \text{ mol } L^{-1}$
- (c)  $0.4 \text{ mol } L^{-1}$
- (d)  $0.6 \text{ mol } L^{-1}$ .
- 17. Before equilibrium is set-up for the chemical reaction,  $N_2O_4 \rightleftharpoons 2NO_2$ , vapour \* density of the gaseous mixture was measured. If D is the theoretical value of vapour



density, variation of x with D/d is shown by the following graph.

What is the value of D/d at point A?

- (a) 0
- (b) 1.5
- (c) 1
- (d) 0.5
- 18. The standard reduction potentials of Mg, Zn, Ni, H<sub>2</sub>, Cu and Ag are -2.37, -0.76, -0.25, 0.00, 0.34 and 0.80 volt respectively. Which one of the following cells has maximum voltage?
  - (a)  $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$
  - (b)  $Cu^{2+} + H_2 \rightarrow Cu + 2H^+$
  - (c) Ni + Cu<sup>2+</sup>  $\rightarrow$  Ni<sup>2+</sup> + Cu
  - (d)  $Zn + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag$
- 19. A compound of Xe and F is found to have 53.5% Xe. What is the oxidation number of Xe in this compound?
- (a) -4 (b) 0 (c) +4
- 20. On adding 0.1 M solution each of Ag<sup>+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup> in a Na<sub>2</sub>SO<sub>4</sub> solution, which species is first precipitated?  $[K_{sp}(BaSO_4) = 10^{-11}, K_{sp}(CaSO_4) = 10^{-6},$  $K_{sp}(Ag_2SO_4) = 10^{-5}$ ]

- (a)  $Ag_2SO_4$
- (b) BaSO<sub>4</sub>
- (c) CaSO<sub>4</sub>
- (d) All of these

#### **SOLUTIONS**

1. (c):  $2PQ \Longrightarrow P_2 + Q_2$ ;  $K_1 = \frac{[P_2][Q_2]}{[PQ]^2} = 2.5 \times 10^5$ 

$$PQ + \frac{1}{2}R_2 \Longrightarrow PQR \; ; \; K_2 = \frac{[PQR]}{[PQ][R_2]^{1/2}} = 5 \times 10^{-3}$$

$$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR$$

$$K_3 = \frac{[PQR]}{[P_2]^{1/2} [Q_2]^{1/2} [R_2]^{1/2}} = \frac{K_2}{\sqrt{K_1}} = \frac{5 \times 10^{-3}}{\sqrt{2.5 \times 10^5}}$$
$$= 1 \times 10^{-5}$$

2. (c): 
$$X_{(g)} + Y_{(g)} \Longrightarrow 3Z_{(g)}$$

$$[X] = 1/3, [Y] = 2/3, [Z] = 4/3$$

$$|X| = 1/3, |Y| = 2/3, |Z| = 4/3$$

$$\Rightarrow Q_c = \frac{\binom{4}{3}^3}{\binom{1}{3}\binom{2}{3}} = 10.66$$

- (a) Since,  $K_c = 10$  i.e.  $Q_c > K_c$ , thus reaction will occur in backward direction.
- (b) Since,  $K_c = 15$  i.e.  $K_c > Q_c$ , thus the reaction will occur in forward direction.
- (c) Since,  $Q_c = K_c$ , reaction is at equilibrium.
- 3. (a):  $Mn^{7+} + 5e^{-} \longrightarrow Mn^{2+}$ ;  $Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$  $M_{eq.}$  of  $KMnO_4 = M_{eq.}$  of  $FeSO_4 \cdot 7H_2O$

$$5.5 \times 0.1 \times 5 = \frac{w}{278} \times 1000 \implies w = 0.7645$$

$$\therefore$$
 % of FeSO<sub>4</sub>·7H<sub>2</sub>O =  $\frac{0.7645}{5} \times 100 = 15.29\%$ 

- 4. (c): We know, pH + pOH = 14
- $\therefore$  pOH of the buffer = 14 10 = 4

For basic buffers,  $pOH = pK_b + log \frac{[Salt]}{[Base]}$ 

$$4 = 4.75 + \log \frac{[Salt]}{[Base]}$$

or 
$$log \frac{[Salt]}{[Base]} = -0.75 \implies \frac{[Salt]}{[Base]} = 0.1778$$

or 
$$\frac{\frac{0.2}{1000} \times 30}{\frac{0.3}{1000} \times V} = 0.1778 \therefore V = 112.5 \text{ mL}$$

5. (a): NaBH<sub>4</sub>: +1+x+4(-1) = 0  $\Rightarrow x = +3$  $K_2 \underline{Ta} F_7 : +2 + x + (-7) = 0 \implies x = +5$ 

$$Mg_2P_2O_7: +4 + 2x + (-14) = 0 \implies x = +5$$
 $Na_2S_4O_6: +2 + 4x + (-12) = 0$ 
or  $4x = 10 \implies x = +2.5$ 

$$N_3H: 3x + 1 = 0 \implies x = -\frac{1}{3}$$

6. (a): Moles of NaOH = 
$$\frac{800 \times 0.05}{1000} = 0.04$$

Moles of HCI = 
$$\frac{200 \times 0.1}{1000} = 0.02$$

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

Initial moles: 0.040.02 Moles after reaction: 0.02 0.02 0.02

Total volume of solution = 800 + 200 = 1000 mL = 1L

$$[OH^-] = \frac{0.02}{1} = 0.02$$

$$pOH = -\log(2 \times 10^{-2})$$

$$pOH = 1.699$$

$$pH = 14 - 1.699 = 12.301$$

7. **(b)**: 
$$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$$
  
Initial moles:  $1 \qquad 0 \qquad 0$ 

Moles at equilibrium: (1 – α)

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\alpha^2(\alpha/2)}{(1-\alpha)^2} \ (\because \alpha <<<1)$$

$$K_c = \frac{\alpha^3}{2} \implies 1 \times 10^{-6} = \frac{\alpha^3}{2}$$

$$\alpha^3 = 2 \times 10^{-6}$$

$$\alpha = (2 \times 10^{-6})^{1/3} = 1.2599 \times 10^{-2} \approx 1.3 \times 10^{-2}$$

% dissociation =  $1.3 \times 10^{-2} \times 100 = 1.3\%$ 

#### 8. (a): $\overrightarrow{ClO_3}$ $\longrightarrow$ $\overrightarrow{Cl_2}$ x - 6 = -1 x = 0

Oxidation number has changed by 5

Equivalent mass = 
$$\frac{\text{Molecular mass}}{\text{Change in oxidation number}} = \frac{84.45}{5}$$
  
= 16.89

9. **(b)**: 
$$A^{n-} \longrightarrow A^{a+} + (a+n)e^{-}$$

$$Cr_2 + 6e^- \longrightarrow 2Cr^{3+}$$

Also  $M_{eq.}$  of  $A = M_{eq.}$  of  $K_2Cr_2O_7$ 

 $3.26 \times 10^{-3} (a + n) = 1.68 \times 10^{-3} \times 6$ 

or  $a+n=3 \implies a=3-n$ 

10. (b):  $CH_3COCH_{3(g)} \rightleftharpoons CH_3CH_{3(g)} + CO_{(g)}$ 

Initial: At eq.: (1-x)

Total moles at equilibrium: (1 + x)

$$x_{\text{CO}} = \frac{x}{1+x} = \frac{1}{3}$$
 :  $x = 0.5$ 

- ∴ Total moles at equilibrium = 1.5
- ∵ Initial pressure = 100 mm of Hg

$$\frac{P_1}{n_1} = \frac{P_2}{n_2} \implies \frac{100}{1} = \frac{P_2}{1.5}$$

∴ Equilibrium pressure = 150 mm of Hg

$$p_{\rm CO} = x_{\rm CO} \cdot p_{\rm T} \Rightarrow 50 \text{ mm of Hg}$$

$$p_{\text{CH}_3\text{CH}_3} = x_{\text{CH}_3\text{CH}_3} \cdot p_{\text{T}} \Rightarrow 50 \text{ mm of Hg}$$

 $p_{\text{CH}_3\text{COCH}_3} = x_{\text{CH}_3\text{COCH}_3} \cdot p_{\text{T}} \Rightarrow 50 \text{ mm of Hg}$ 

$$K_p = \frac{p_{\text{CH}_3\text{CH}_3} \cdot p_{\text{CO}}}{p_{\text{CH}_3\text{COCH}_3}} = 50 \text{ mm of Hg}$$

11. (c): If α is the degree of dissociation at certain temperature under the atmospheric pressure, then

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial conc.: At equilibrium :  $1 - \alpha$ 

Now, 
$$K_p = \frac{\alpha^2}{1 - \alpha^2} P$$

Putting P = 1 atm and  $\alpha = 0.2$ 

$$K_p = \frac{(0.2)^2}{1 - (0.2)^2} \times 1 = 0.04$$

When  $\alpha = \frac{1}{2} = 0.5$ , then let pressure is P'

$$K_P = \frac{\alpha^2}{1 - \alpha^2} \cdot P' \Rightarrow 0.04 = \frac{(0.5)^2 P'}{1 - (0.5)^2}$$

$$P' = \frac{(0.04)[1 - (0.5)^2]}{(0.5)^2} = 0.12 \text{ atm}$$

$$P' = \frac{(0.04)[1 - (0.5)^2]}{(0.5)^2} = 0.12 \text{ atm}$$

#### 12. (a)

13. (a): The reducing agent itself gets oxidised i.e., the oxidation number increases.

(1) 
$$H_2O_2^{-1} + 2H^+ + 2e^- \longrightarrow 2H_2O^{-2}$$

(2) 
$$H_2O_2 - 2e^- \longrightarrow O_2 + 2H^+$$

(3) 
$$H_2^{-1}O_2 + 2e^- \longrightarrow 2OH^-$$

(4) 
$$H_2O_2^{-1} + 2OH^- - 2e^- \longrightarrow O_2 + 2H_2O$$

14. (c): 
$$AgIO_3 \rightleftharpoons Ag^+ + IO_3^-$$

s s 
$$[s = Solubility]$$

$$K_{sp} = s^2$$
  
or,  $s^2 = 1.0 \times 10^{-8}$  or,  $s = 1.0 \times 10^{-4} \text{ mol/L}$ 

or, 
$$s = 1.0 \times 10^{-4}$$
 or,  $s = 1.0 \times 10^{-4}$  mol/L  
=  $1.0 \times 10^{-4} \times 283$  g/L (: 1 mol/AgIO<sub>3</sub> = 283 g)

 $\therefore$  1 L or 1000 mL contain  $1.0 \times 10^{-4} \times 283$  g of AgIO<sub>3</sub>

$$\therefore 100 \text{ mL} = \frac{1.0 \times 10^{-4} \times 283}{1000} \times 100$$

$$= \frac{1.0 \times 10^{-4} \times 283 \times 100}{1000} \text{ g/100mL}$$

$$= 28.3 \times 10^{-4} \text{ g/100 mL} = 2.83 \times 10^{-3} \text{ g/100 mL}$$

15. (d): The redox reaction involving the oxidation of  $Fe^{2+}$  (from ferrous ammonium sulphate) is  $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$  Mol. wt. of ferrous ammonium sulphate,

 $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2 O = 392$ 

.. Molarity of FeSO<sub>4</sub>·(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O
$$= \frac{\text{Wt.}}{\text{Mol. wt.}} \times \frac{1000}{\text{Volume}} = \frac{3.92}{392} \times \frac{1000}{100} = 0.1$$

Applying molarity equation,

$$\frac{M_1V_1}{n_1} \text{ (Ferrous ammonium sulphate)} = \frac{M_2V_2}{n_2} \text{(KMnO}_4\text{)}$$

or, 
$$\frac{0.1 \times 20}{5} = \frac{M_2 \times 18}{1}$$
 or  $M_2 = \frac{0.1 \times 20}{5 \times 18} = \frac{1}{45}$ 

Amount of KMnO<sub>4</sub> present in one litre

= Molarity × Mol. wt.(KMnO<sub>4</sub>) = 
$$\frac{1}{45}$$
 × 158 = 3·51 g

16. (c): 
$$SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$$
  
Initial conc.  $1 \quad 1 \quad 1 \quad 1$   
At equilibrium  $1-x \quad 1-x \quad 1+x \quad 1+x$ 

$$K_c = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4 \text{ or } x = 0.6$$

$$[NO_2] = 1 - x = 1 - 0.6 = 0.4 \text{ mol } L^{-1}$$

#### 17. (c): $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

Degree of dissociation,  $\alpha = \frac{D-d}{d}$  or  $\alpha = \frac{D}{d} - 1$ At A,  $\alpha = 0$ 

$$\therefore \quad \frac{D}{d} - 1 = 0 \quad \text{or} \quad \frac{D}{d} = 1$$

18. (a): 
$$Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$$

$$E_{\text{cell}}^{\circ} = E_c - E_a = 0.80 - (-2.37) = +3.17 \text{ V}$$

$$Cu^{2+} + H_2 \rightarrow Cu + 2H^+$$

$$E_{\text{cell}}^{\circ} = 0.34 - 0.00 = +0.34 \text{ V}$$

$$Ni + Cu^{2+} \rightarrow Ni^{2+} + Cu$$

$$E_{\text{cell}}^{\circ} = 0.34 - (-0.25) = 0.59$$

$$Zn + 2Ag^{+} \rightarrow Zn^{2+} + 2Ag$$

$$E_{\text{cell}}^{o} = 0.80 - (-0.76 \text{ V}) = 1.56 \text{ V}$$

#### 19. (d):

Element	%	At. mass	Relative	Simplest
			number of	ratio
			moles	
Xe	53.5	131	0.408	1
F	46.5	19	2.44	6

- ... The empirical formula is XeF<sub>6</sub>.
- .. Oxidation state of Xe is +6.

**20. (b)**: For  $Ag_2SO_4$ ;  $K_{sp} = [Ag^+]^2 [SO_4^{2-}]$ 

:. [SO<sub>4</sub><sup>2-</sup>] needed for precipitation of

$$Ag_2SO_4 > \frac{K_{sp}}{[Ag^+]^2} = \frac{10^{-5}}{0.1 \times 0.1} = 10^{-3} M$$

$$SO_4^{2-} > 10^{-3} M$$

For CaSO<sub>4</sub>;  $K_{sp} = [Ca^{2+}][SO_4^{2-}]$ 

 $\therefore$  [SO<sub>4</sub><sup>2-</sup>] needed for precipitation of

$$CaSO_4 > \frac{K_{sp}}{[Ca^{2+}]} = \frac{10^{-6}}{0.1} = 10^{-5} M$$

For BaSO<sub>4</sub>; 
$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = \frac{10^{-11}}{0.1} = 10^{-10}$$

$$\therefore$$
 SO<sub>4</sub><sup>2-</sup> needed for precipitation of BaSO<sub>4</sub> >  $\frac{K_{sp}}{[\text{Ba}^{2+}]}$   
SO<sub>4</sub><sup>2-</sup> > 10<sup>-10</sup> M

Thus, minimum  $[SO_4^{2-}]$  is required for precipitation of BaSO<sub>4</sub> and hence it is precipitated out first.

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Series 4

#### **Equilibrium I Redox Reactions**

Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

- All questions are compulsory.
- (ii) Section A: Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
- (iii) Section B: Q. no. 21 to 27 are short answer questions and carry 2 marks each.
- (iv) Section C: Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
- (v) Section D: Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
- (vi) There is no overall choice in the question paper. However, internal choices are given in the sections.
- (vii) Use log tables if necessary, use of calculators is not allowed.

#### SECTION-A

- 1. A compound contains atoms X, Y and Z. The oxidation number of X is +2, Y is +5 and Z is -2. The possible formula of the compound is
  - (a)  $XYZ_2$
- (b)  $Y_2(XZ_3)_2$
- (c)  $X_3(YZ_4)_2$  (d)  $X_3(Y_4Z)_2$
- The dissociation constants for acetic acid and HCN at 25 °C are  $1.5 \times 10^{-5}$  and  $4.5 \times 10^{-10}$  respectively. The equilibrium constant for the reaction,  $CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ 
  - (a)  $3.0 \times 10^{-5}$  (b)  $3.0 \times 10^{-4}$
  - (c)  $3.0 \times 10^4$

would be

- (d)  $3.0 \times 10^5$
- 3. The equilibrium constant  $(K_c)$  for the reaction  $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$  at temperature T is  $4 \times 10^{-4}$ . The value of  $K_c$  for the reaction,
  - $NO_{(g)} \rightarrow \frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)}$  at the same temperature is

- (a)  $2.5 \times 10^2$
- (b)  $4 \times 10^{-4}$
- (c) 50.0
- (d) 0.02
- Equivalent weight of MnO<sub>4</sub> in acidic, basic and neutral medium are in the ratio of
  - (a) 3:5:15
- (b) 5:3:1
- (c) 5:1:3 (d) 3:5:5
- Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be
  - (a)  $3.98 \times 10^8$  (b)  $3.88 \times 10^6$
  - (c)  $3.68 \times 10^{-6}$ 
    - (d)  $3.98 \times 10^{-6}$
- 6. The brown ring complex compound is formulated as  $[Fe(H_2O)_5NO]SO_4$ . The oxidation state of Fe is
  - (a) +1
- (b) +2 (c) +3
- (d) zero
- 1 M NaCl and 1 M HCl are present in an aqueous solution. The solution is
  - (a) not a buffer solution with pH < 7
  - (b) not a buffer solution with pH > 7
  - (c) a buffer solution with pH < 7
  - (d) a buffer solution with pH > 7.

- 8. Amongst the following identify the species with an atom in +6 oxidation state.

  - (a)  $MnO_4$  (b)  $[Cr(CN)_6]^{3-}$  (c)  $[NiF_6]^{2-}$  (d)  $CrO_2Cl_2$
- 9. The Henderson's equation for acetic acid and sodium acetate buffer is given by the expression

(a) 
$$pH = pK_a - log \frac{[CH_3COONa]}{[CH_3COOH]}$$

(b) 
$$pH = pK_a + log \frac{[CH_3COONa]}{[CH_3COOH]}$$

(c) 
$$pOH = pK_a - log \frac{[CH_3COONa]}{[CH_3COOH]}$$

(d) 
$$pOH = pK_a - log \frac{[CH_3COOH]}{[CH_3COONa]}$$

10. In the reaction,

$$3Br_2 + 6CO_3^{2-} + 3H_2O \rightarrow 5Br^- + BrO_3^- + 6HCO_3^-$$

- (a) bromine is oxidised and carbonate is reduced
- (b) bromine is reduced and water is oxidised
- (c) bromine is neither oxidised and reduced
- (d) bromine is both oxidised and reduced.
- 11. What does the equilibrium constant K < 1 show?
- 12.  $K_c$  for the reaction,  $N_2 + 3H_2 \rightleftharpoons 2NH_3$  is  $0.5 \text{ mol}^{-2} L^2$ at 400 K. Find  $K_p$ . (Given R = 0.0821 litre atm  $deg^{-1} mol^{-1}$ ).
- 13. Calculate the oxidation number of phosphorus in the following species:
  - (a)  $HPO_3^{2-}$
- (b)  $PO_4^{3-}$
- 14. Write down the conjugate base of  $[Al(H_2O)_6]^{3+}$ .
- 15. Calculate the oxidation number of nitrogen in nitrous acid and nitric acid.
- 16. The reaction quotient of a reversible reaction is  $Q_c$ and the equilibrium constant is  $K_c$ . What do you conclude from the reaction if  $Q_c < K_c$ ?
- 17. A tank is full of water. Water is coming in as well as going out at the same rate. What will happen to the level of water in the tank? What is the name given to such state?
- 18. Is it possible to get precipitate of  $Fe(OH)_3$  at pH = 2?
- 19. In the given reaction, identify the species undergoing oxidation and reduction:

$$2 \text{HgCl}_{2(aq)} + \text{SnCl}_{2(aq)} \longrightarrow \text{Hg}_2 \text{Cl}_{2(s)} + \text{SnCl}_{4(aq)}$$

20. Write the expression for the equilibrium constant  $K_c$  for the following equilibrium:

$$3Fe_{(s)} + 4H_2O_{(g)} \Longrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$$

#### SECTION-B

- 21. The value of  $K_w$  is 9.55  $\times$  10<sup>-14</sup> at a certain temperature. Calculate the pH of water at this temperature.
- **22.** The value of  $K_c$  for the reaction,

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)} \text{ is } 1 \times 10^{-4}.$$

At a given time, the composition of reaction mixture

[HI] =  $2 \times 10^{-5}$  mol, [H<sub>2</sub>] =  $1 \times 10^{-5}$  mol and  $[I_2] = 1 \times 10^{-5}$  mol. In which direction will the reaction proceed?

- 23. Write chemical reaction to justify that hydrogen peroxide can act as oxidizing as well as reducing agent.
- 24. MnO<sub>4</sub><sup>2-</sup> undergoes disproportionation reaction in acidic medium but MnO<sub>4</sub> does not. Give reason.

#### OR

Which of the following are oxidising agents and reducing agents? Justify your answer with half equations. Br<sub>2</sub>, Fe<sup>3+</sup>, I<sup>-</sup>, Na.

25. Balance the following equation in basic medium by ion-electron method:

$$Cl_2O_{7(g)} + H_2O_{2(aq)} \longrightarrow ClO_{2(aq)}^- + O_{2(g)}$$
(KVS, NCT 2011)

26. Urine has a pH of 6.0. If a patient eliminates 1300 mL of urine per day, how many gram equivalents of the acid he eliminates per day?

#### OR

- (i) Magnesium is not precipitated from a solution of its salt by NH<sub>4</sub>OH in the presence of NH<sub>4</sub>Cl. Why?
- (ii) Calculate the pH of 2 g of TlOH dissolved in water to give 2 L of solution (At. mass of Tl = 204.384).
- 27. An iron rod is immersed in a solution containing 1.0 M NiSO<sub>4</sub> and 1.0 M ZnSO<sub>4</sub>. Predict giving reasons which of the following reactions is likely to proceed:
  - (i) Fe reduces Zn<sup>2+</sup> ions
  - (ii) Fe reduces Ni<sup>2+</sup> ions

(Given: 
$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$$
,  $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V}$  and  $E_{\text{Ni}^{2+}/\text{Ni}}^{\circ} = -0.25 \text{ V}$ )

#### SECTION-C

28. Balance the following equation by oxidation number method.

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow$$
 $Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$ 

29. The solubility product of  $Al(OH)_3$  is  $2.7 \times 10^{-11}$ . Calculate its solubility in g L<sup>-1</sup> and also find out pH of this solution. (Atomic mass of Al = 27 u).

#### OR

At 473 K, equilibrium constant  $K_c$  for the decomposition of phosphorus pentachloride, PCl<sub>5</sub> is  $8.3 \times 10^{-3}$ . If decomposition is depicted as:

PCl<sub>5(g)</sub>  $\rightleftharpoons$  PCl<sub>3(g)</sub> + Cl<sub>2(g)</sub>;  $\Delta_r H^o = 124.0 \text{ kJ mol}^{-1}$ 

- (i) What is the value of  $K_c$  for the reverse reaction at the same temperature?
- (ii) What would be the effect on  $K_c$  if (a) the pressure is increased (b) the temperature is increased?
- 30. Is it possible to store:
  - (i) copper sulphate solution in a zinc vessel?
  - (ii) copper sulphate solution in a silver vessel?
  - (iii) copper sulphate solution in a gold vessel?

(Given: 
$$E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}; E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V};$$
  
 $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V} \text{ and } E^{\circ}_{\text{Au}^{3+}/\text{Au}} = +1.40 \text{ V})$ 

- 31. Equal volumes of 0.002 M solutions of sodium iodate and copper chlorate are mixed together. Will it lead to precipitation of copper iodate? (For copper iodate,  $K_{sp} = 7.4 \times 10^{-8}$ )
- 32. Determine the pH of  $10^{-8}$  M HCl solution. (log 11 = 1.0414). (KVS 2016, NCT 2016, 2017)

#### OR

(a) The concentration of hydrogen ions in a sample of soft drink is  $3.8 \times 10^{-3}$  M. What is its pH? (log 3.8 = 0.58)

(NCERT, KVS 2008, NCT 2014)

(b) State Le-Chatelier's principle.

(NCT 2015, KVS 2016)

- 33. Both Cr<sub>2</sub>O<sup>2-</sup><sub>7(aq)</sub> and MnO<sup>-</sup><sub>4(aq)</sub> can be used to titrate Fe<sup>2+</sup><sub>(aq)</sub>. If in a given titration, 24.50 cm<sup>3</sup> of 0.1 M Cr<sub>2</sub>O<sup>2-</sup><sub>7</sub> were used, then what volume of 0.1 M MnO<sup>-</sup><sub>4</sub> solution would have been used for the same titration?
- 34. Copper dissolves in dilute nitric acid but not in dilute HCl. Explain.

#### SECTION-D

- 35. Explain the following:
  - (i) It is not possible to determine the absolute value of single electrode potential.
  - (ii) Iron undergoes oxidation more readily than copper.
  - (iii)In an electrochemical cell, an electrode with lower electrode potential acts as a reducing agent.
  - (iv) When a copper rod is placed in silver nitrate solution, the solution becomes hot but the reverse is not true.
  - (v) Iron reacts with dilute H<sub>2</sub>SO<sub>4</sub> to evolve H<sub>2</sub> gas but Ag does not.

#### OR

Write the following redox reactions using half equations:

(i) 
$$Zn_{(s)} + PbCl_{2(aq)} \longrightarrow Pb_{(s)} + ZnCl_{2(aq)}$$

(ii) 
$$2Fe_{(aq)}^{3+} + 2I_{(aq)}^{-} \longrightarrow I_{2(s)} + 2Fe_{(aq)}^{2+}$$

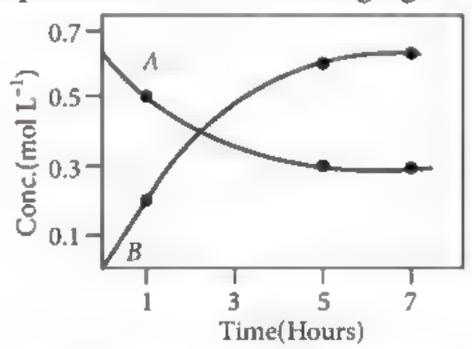
(iii) 
$$2Na_{(s)} + Cl_{2(g)} \longrightarrow 2NaCl_{(s)}$$

(iv) 
$$Mg_{(s)} + Cl_{2(g)} \longrightarrow MgCl_{2(s)}$$

(v) 
$$Zn_{(s)} + 2H_{(aq)}^+ \longrightarrow Zn_{(aq)}^{2+} + H_{2(g)}$$

In each of the reactions given above, mention

- (a) which reactant is oxidized? To what?
- (b) which reactant is the oxidiser?
- (c) which reactant is reduced? To what?
- (d) which reactant is the reducer?
- 36. (i) The progress of the reaction,  $A \rightleftharpoons nB$ , with time is represented in the following figure:



On the basis of above graph, determine:

- (a) the value of n
- (b) the equilibrium constant, K.
- (ii) (a) Ammonium chloride is acidic in liquid ammonia solvent. Explain, why?
- (b) Why does solubility of CO<sub>2</sub> decrease with rise in temperature?

#### OR

- (i) A sample of AgCl was treated with 5.00 mL of 1.5 M Na<sub>2</sub>CO<sub>3</sub> solution to give Ag<sub>2</sub>CO<sub>3</sub>. The remaining solution contained 0.0026 g of Cl per litre. Calculate the solubility product of AgCl.  $(K_{sp} \text{ for } Ag_2CO_3 = 8.2 \times 10^{-12})$ .
- (ii) The solubility of  $Pb(OH)_2$  in water is  $6.7 \times 10^{-6}$  M. Calculate the solubility of  $Pb(OH)_2$  in a buffer solution of pH = 8.
- 37. (i)  $K_p$  for the reaction  $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$  at 400 °C is  $1.64 \times 10^{-4}$  atm<sup>-2</sup>. Find  $K_c$ . Also calculate  $\Delta G^\circ$  using  $K_p$  and  $K_c$  values.
  - (ii) Under what conditions,  $K_c = K_p$  for a gaseous reactions? Give one example.

#### OR

- (i) 0.15 mole of pyridinium chloride has been added to 500 cm<sup>3</sup> of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in the volume ( $K_b$  for pyridine =  $1.5 \times 10^{-9}$ ).
- (ii) Describe the effect of (a) addition of H<sub>2</sub>
   (b) addition of CH<sub>3</sub>OH (c) removal of CO
   (d) removal of CH<sub>3</sub>OH, on the equilibrium of the reaction: 2H<sub>2(g)</sub> + CO<sub>(g)</sub> = CH<sub>3</sub>OH<sub>(g)</sub>

#### SOLUTIONS

- 1. (c): Sum of the oxidation numbers of atoms in it is zero.
- 2. (c) : Given,  $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$   $K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.5 \times 10^{-5}$

 $HCN \rightleftharpoons H^+ + CN^-$ 

$$K_2 = \frac{[\text{CN}^-][\text{H}^+]}{[\text{HCN}]} = 4.5 \times 10^{-10}$$

CN<sup>-</sup> + CH<sub>3</sub>COOH ⇒ HCN + CH<sub>3</sub>COO<sup>-</sup>

$$K = \frac{[\text{HCN}][\text{CH}_3\text{COO}^-]}{[\text{CN}^-][\text{CH}_3\text{COOH}]}$$

$$K = \frac{K_1}{K_2} = \frac{1.5 \times 10^{-5}}{4.5 \times 10^{-10}} \approx 0.3 \times 10^5 \text{ or } K = 3 \times 10^4$$

3. (c):  $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ ;  $K_c = 4 \times 10^{-4}$  ...(i)

On multiplying the equation (i) by  $\frac{1}{2}$ , we get

$$\frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow NO_{(g)}; K'_{c} \qquad ...(ii)$$

$$K'_{c} = \sqrt{K_{c}} = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2}$$

On reversing the equation (ii), we get

$$NO_{(g)} \rightarrow \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}; K''_c$$

$$K_{\epsilon}'' = \frac{1}{K_{\epsilon}'} = \frac{1}{2 \times 10^{-2}} = 50.0$$

4. (d): Acidic medium:

$$MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O$$

Basic medium:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

Neutral medium:

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$$

If M is the molecular weight of KMnO<sub>4</sub>, then its equivalent weights in acidic, basic, and neutral medium are respectively:

$$\frac{M}{5}: \frac{M}{3}: \frac{M}{3}$$
 or 3:5:5.

5. (d):  $pH = -\log[H^+]$ 

 $[H^+]$  = antilog (-pH) = antilog(-5.4) = 3.98 × 10<sup>-6</sup>

6. (a): NO in iron complexes has oxidation number equal to one.

$$x + 5 \times 0 + 1 - 2 = 0$$
,  $x = +1$ .

- 7. (a): HCl is a strong acid and its salt does not form buffer solution. As the resultant solution is acidic, hence pH is less than 7.
- 8. (d): Oxidation numbers are

Mn in MnO $_4^-$  is + 7

Cr in 
$$[Cr(CN)_6]^{3-}$$
 is +3  $(x-6=-3 \text{ or } x=+3)$ 

Ni in 
$$[NiF_6]^{2-}$$
 is +4  $(x-6=-2 \text{ or } x=+4)$ 

and Cr in 
$$CrO_2Cl_2$$
 is +6  $(x + 2 \times (-2) + 2 \times (-1) = 0$ 

or 
$$x - 4 - 2 = 0 \implies x = +6$$
.

9. (b)

10. (d):

$$^{0}_{3}Br_{2}^{0}+6CO_{3}^{2-}+3H_{2}O\rightarrow 5Br^{-}+BrO_{3}^{-}+6HCO_{3}^{-}$$

Here, bromine is both oxidised and reduced

11. It shows that reaction is moving in backward direction. i.e., it is far from completion.

12. 
$$K_p = K_c (RT)^{\Delta n_g}$$

$$\Delta n_g = (n_P - n_R) = (2 - 4) = -2$$

$$K_p = 0.5 \times (0.082 \times 400)^{-2}$$
;  $K_p = 4.648 \times 10^{-4} \text{ atm}^{-2}$ 

13. (a) 
$$HPO_3^{2^-} = +1 + x + (-6) = -2$$
 :  $x = +3$ 

**(b)** 
$$PO_4^{3-} = x + (-8) = -3$$
 :  $x = +5$ 

14. 
$$[Al(H_2O)_6]^{3+} \stackrel{H_2O}{\rightleftharpoons} [Al(OH)(H_2O)_5]^{2+} + H_3O^+$$
Acid Conjugate base

15. Nitrous acid i.e., HNO<sub>2</sub>

$$+1 + x - 2 \times 2 = 0$$
;  $x = +3$ 

Nitric acid i.e., HNO3

$$+1 + x - 2 \times 3 = 0$$
;  $x = +5$ 

- 16. If  $Q_c < K_c$ , the reaction tends towards forward direction to attain equilibrium.
- 17. It will remain same because rate of inflow is equal to rate of outflow. The state is called 'equilibrium'.
- 18. No, because Fe(OH)<sub>3</sub> will dissolve in strongly acidic medium.

Reduction
$$\begin{array}{c}
 & \downarrow \\
 & \downarrow$$

SnCl<sub>2</sub> is oxidised and HgCl<sub>2</sub> is reduced.

20. 
$$K_c = \frac{[H_{2(g)}]^4 [Fe_3 O_{4(s)}]}{[Fe_{(s)}]^3 [H_2 O_{(g)}]^4} = \frac{[H_{2(g)}]^4}{[H_2 O_{(g)}]^4}$$

(: concentration of solids is taken as unity.)

21. 
$$K_w = 9.55 \times 10^{-14}$$

For water,  $[H_3O^+] = [OH^-]$  and

$$K_{w} = [H_{3}O^{+}][OH^{-}] = 9.55 \times 10^{-14}$$

or 
$$[H_3O^+][H_3O^+] = 9.55 \times 10^{-14}$$

$$[H_3O^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7} \text{ M}$$

$$pH = -log(3.09 \times 10^{-7})$$

$$= -(\log 3.09 + \log 10^{-7}) = -(0.489 - 7) = 6.51$$

22. 
$$Q_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{(1 \times 10^{-5}) \times (1 \times 10^{-5})}{(2 \times 10^{-5})^2} = \frac{1}{4}$$
  
= 0.25 = 2.5 × 10<sup>-1</sup>

Value of  $K_c = 1 \times 10^{-4}$ 

Since  $Q_c > K_c$ , the reaction will proceed in reverse direction.

23. The O.N. of O in  $H_2O_2$  is -1. It can increase its oxidation number to zero and acts as a reducing agent. It can also decrease its oxidation number to -2 and acts as an oxidising agent.

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$$
  
 $(H_2O_2 \text{ is acting as a reducing agent.})$   
 $H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O$   
 $(H_2O_2 \text{ is acting as an oxidising agent.})$ 

24. In  $MnO_4^-$ , Mn has its highest oxidation state *i.e.*, +7. Hence, it does not undergo disproportionation reaction.  $MnO_4^{2-}$  has +6 oxidation state and can undergo disproportionation since it can adopt lower and higher oxidation state.

$$3 \text{MnO}_4^{2-} + 4 \text{H}^+ \longrightarrow 2 \text{MnO}_4^{-} + \frac{4}{\text{MnO}_2} + 2 \text{H}_2 \text{O}$$

Manganate ion

Permanganate ion

OR

 $Br_2 + 2e^- \rightarrow Br^-$ : Reduction

(Oxidising agent)

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$$
: Reduction

(Oxidising agent)

$$2I^- \rightarrow I_2 + 2e^-$$
: Oxidation

(Reducing agent)

$$Na \rightarrow Na^+ + e^-$$
: Oxidation

(Reducing agent)

25. Oxidation half-reaction:

$$H_2O_{2(aq)} + 2OH_{(aq)}^- \rightarrow O_{2(g)} + 2H_2O_{(l)} + 2e^-] \times 4$$
 ...(i)

Reduction half-reaction:

$$Cl_2O_{7(g)} + 3H_2O_{(l)} + 8e^- \rightarrow 2ClO_{2(aq)}^- + 6OH_{(aq)}^-$$
 ...(ii)

Adding eq. (i) and (ii)

$$Cl_2O_{7(g)} + 4H_2O_{2(aq)} + 2OH_{(aq)}^- \rightarrow 2ClO_{2(aq)}^- + 4O_{2(g)} + 5H_2O_{(l)}$$

**26.** 
$$\because$$
 pH = 6.0

$$\therefore [H_3O^+] = 10^{-6} M$$

i.e., [Acid] = 
$$10^{-6}$$
 M =  $10^{-6}$  N

Thus, 1000 mL of the urine contain acid =  $10^{-6}$  g eq.

- :. 1300 mL of the urine will contain acid =  $1.3 \times 10^{-6}$  g eq.
- (i) The solubility product of Mg(OH)<sub>2</sub> is high. Presence of NH<sub>4</sub>Cl suppresses the dissociation of NH<sub>4</sub>OH due to common ion effect thus giving low concentration of [OH<sup>-</sup>]. The ionic product, therefore, cannot exceed the solubility product.
- (ii) Molarity of TlOH

= 
$$\frac{\text{Given mass}}{\text{Molecular mass}} \times \frac{1}{\text{Volume of solution (in litres)}}$$
  
=  $\frac{22}{221.38} \times \frac{1}{2} = 0.0045 \text{ mol L}^{-1}$ 

Assuming complete ionisation of TlOH,

$$[OH^{-}] = 0.0045 \text{ mol } L^{-1}$$

So, 
$$[H^+] = K_w/[OH^-] = 2.22 \times 10^{-12}$$
  
pH =  $-\log [H^+] = 11.65$ 

- 27. (i) Since,  $E^{\circ}$  of Zn is more negative than that of Fe, therefore, Zn is more likely to be oxidised than Fe. In other words, Fe rod will not reduce  $Zn^{2+}$  ions.
- (ii) Since, E° of Fe is more negative than that of Ni, therefore, Fe will be oxidised to Fe<sup>2+</sup> ions while Ni<sup>2+</sup> ions will be reduced to Ni. Thus, Fe reduces Ni<sup>2+</sup> ions.

28. 
$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow Cr_2(SO_4)_3 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

Change in oxidation number has occurred in chromium and iron.

$$K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3$$
 ...(i)  
 $^{+2}_{2FeSO_4} \rightarrow Fe_2(SO_4)_3$  ...(ii)

Decrease in oxidation number of Cr per molecule = 6 Increase in oxidation number of Fe per molecule = 1Hence, multiplying eq. (ii) by 3 and adding in eq. (i),  $K_2Cr_2O_7 + 6FeSO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3$ To balance potassium ions and sulphate ions 1 molecule of K<sub>2</sub>SO<sub>4</sub> is added to R.H.S. and 7 molecules of H<sub>2</sub>SO<sub>4</sub> are added to L.H.S.

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow$$
 $Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4$ 

To balance hydrogen and oxygen, 7H2O should be added on R.H.S. Hence, the balanced equation is

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

29. 
$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^{-1}$$
  
Conc. at  $t = 0$  1 0 0  
Conc. at equilibrium  $1 - S$   $S$  3S  
 $K_{sp} = [Al^{3+}][OH^{-}]^3 = (S)(3S)^3 = 27S^4$   
 $S^4 = \frac{K_{sp}}{27} = \frac{2.7 \times 10^{-11}}{27} = 1 \times 10^{-12}$ 

 $S = 1 \times 10^{-3} \text{ mol L}^{-1}$ 

Molar mass of  $Al(OH)_3 = 78 g$ 

.. Solubility of 
$$Al(OH)_3$$
 in g  $L^{-1} = 1 \times 10^{-3} \times 78$   
=  $78 \times 10^{-3} = 7.8 \times 10^{-2}$  g  $L^{-1}$ 

pH of the solution :  $S = 1 \times 10^{-3} \text{ mol L}^{-1}$  $[OH^{-}] = 3S = 3 \times 1 \times 10^{-3} = 3 \times 10^{-3}$  $pOH = -log[OH^{-}] = -log(3 \times 10^{-3})$ pOH = 3 - log 3 = 3 - 0.4771 = 2.523pH = 14 - pOH = 14 - 2.523 = 11.47

(i) For the reverse reaction:  $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$  $K_c' = \frac{1}{K_c} = \frac{1}{8.3 \times 10^{-3}} = 120.48$ 

(ii) (a) The value of equilibrium constant is constant for a particular reaction at a particular temperature hence, increase in pressure will have no effect.

(b) As the reaction is endothermic, the increase in temperature will favour the forward reaction. More  $PCl_5$  will dissociate to form  $PCl_3$  and  $Cl_2$  hence,  $K_c$  will increase.

30. (i) We cannot place CuSO<sub>4</sub> solution in a zinc vessel, because Zn ( $E^{\circ} = -0.76 \text{ V}$ ) is stronger reducing agent than  $Cu(E^{\circ} = +0.34 \text{ V})$ . So, Zn can displace Cu from its salt solution.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

(ii) We can store CuSO<sub>4</sub> solution in a silver vessel, because Ag ( $E^{\circ} = +0.80 \text{ V}$ ) is stronger oxidising agent than Cu ( $E^{\circ} = +0.34 \text{ V}$ ). So, Ag cannot displace Cu from its salt solution.

(iii) We can store CuSO<sub>4</sub> solution in a gold vessel, because Au ( $E^{\circ} = +1.40 \text{ V}$ ) is stronger oxidising agent than Cu ( $E^{\circ} = +0.34 \text{ V}$ ). So, Au cannot displace Cu from its salt solution.

31. When equal volumes of sodium iodate and copper chlorate are mixed, the molar concentrations of both the solutes would be reduce to half i.e., 0.001 M.

NaIO<sub>3</sub> 
$$\longrightarrow$$
 Na<sup>+</sup> + IO<sub>3</sub><sup>-</sup>  
0 001 M 0.001 M  
Cu(ClO<sub>3</sub>)<sub>2</sub>  $\longrightarrow$  Cu<sup>2+</sup> + 2ClO<sub>3</sub><sup>-</sup>  
0.001 M 0.001 M

 $\therefore$  After mixing,  $[IO_3^-] = [NaIO_3] = 0.001 M$  $[Cu^{2+}] = [Cu(IO_3)_2] = 0.001 M$ 

Solubility equilibrium for copper iodate may be written as,

$$Cu(IO_3)_{2(s)} \rightleftharpoons Cu_{(aq)}^{2+} + 2IO_{3(aq)}^{-}$$
  
Ionic product of copper iodate
$$= [Cu^{2+}] [IO_3^{-}]^2 = (0.001) (0.001)^2 = 1 \times 10^{-9}$$
Since ionic product  $(1 \times 10^{-9})$  is less than  $K_{sp}(7.4 \times 10^{-8})$ , therefore, no precipitation will take place.

32. If we use the relation,  $pH = -\log [H_3O^+]$ , we get pH equal to 8. But this is not correct because an acidic solution cannot have pH greater than 7. It may be noted that in very dilute acidic solutions, when H<sup>+</sup> concentration from acid and water are comparable, the concentration of H<sup>+</sup> from water cannot be neglected. Therefore,

$$[H^+]_{Total} = [H^+]_{acid} + [H^+]_{water}$$
  
Since HCl is strong acid and is completely ionised  
 $[H^+]_{HCl} = 1.0 \times 10^{-8} \text{ M}$ 

The concentration of H<sup>+</sup> from ionisation of water is equal to the [OH] from water,

$$[H^{+}]_{H_{2}O} = [OH^{-}]_{H_{2}O} = x M \text{ (Let)}$$

$$[H^{+}]_{total} = (1.0 \times 10^{-8} + x) M$$
But  $[H^{+}][OH^{-}] = 1.0 \times 10^{-14}$ 

$$\therefore (1.0 \times 10^{-8} + x) (x) = 1.0 \times 10^{-14}$$

$$\Rightarrow x^{2} + 10^{-8} x - 10^{-14} = 0$$
On solving for  $x$ , we get  $x = 9.5 \times 10^{-8}$ 

$$\therefore [H^{+}] = 1.0 \times 10^{-8} + 9.5 \times 10^{-8}$$

$$= 10.5 \times 10^{-8} + 9.5 \times 10^{-7}$$

$$pH = -\log[H^{+}] = -\log(1.05 \times 10^{-7}) = 6.98$$

OR

(a) 
$$[H^+] = 3.8 \times 10^{-3} M$$
  
 $pH = -\log[H^+] = -\log(3.8 \times 10^{-3})$   
 $= 3 \log 10 - \log 3.8 = 3 - 0.5797$   
 $pH = 2.4203 \approx 2.42$ 

- (b) When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.
- 33. The balanced redox reactions involving oxidation of  $Fe^{2+}$  ions by  $Cr_2O_7^{2-}$  and  $MnO_4^-$  respectively are:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$
  
 $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ 

Suppose  $V_2$  cm<sup>3</sup> of  $M_2$  M Fe<sup>2+</sup> is titrated against 24.50 cm<sup>3</sup> of 0.1 M Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and  $V_1$  cm<sup>3</sup> of 0.1 M MnO<sub>4</sub><sup>-</sup> solutions, then,

$$\frac{24.5 \times 0.1}{1} (Cr_2O_7^{2-}) = \frac{M_2V_2}{6} (Fe^{2+}) \qquad ...(i)$$
and 
$$\frac{V_1 \times 0.1}{1} (MnO_4^-) = \frac{M_2V_2}{5} (Fe^{2+}) \qquad ...(ii)$$

Equating (i) and (ii),  $V_1 = 24.5 \times \frac{6}{5} = 29.4 \text{ cm}^3$ 

- 34. Since  $E^{\circ}$  of  $Cu^{2+}/Cu$  electrode (+ 0.34 V) is higher than that of  $H^{+}/H_{2}$  electrode (0.0 V), therefore,  $H^{+}$  ions cannot oxidise Cu to  $Cu^{2+}$  ions and hence Cu dissolved in dil. HCl. In contrast, the electrode potential of  $NO_{3}^{-}$  ion, *i.e.*,  $NO_{3}^{-}$  /NO electrode (+ 0.97 V) is higher than that of copper electrode and hence it can oxidise Cu to  $Cu^{2+}$  ions and hence Cu dissolves in dil. HNO<sub>3</sub>. Thus, Cu dissolves in dil. HNO<sub>3</sub> due to oxidation of Cu by  $NO_{3}^{-}$  ions and not by  $H^{+}$  ions.
- 35. (i) The potential difference between two electrodes can be determined by connecting them to a voltmeter. Therefore, it is not possible to determine the potential of a single electrode because a single electrode constitutes a half-cell and a half-cell reaction cannot take place independently.

An electrode in a half cell cannot lose or gain electrons by itself. For transfer of electrons, one half cell has to be connected to some other half cell. Thus, we cannot determine the absolute value of electrode potential of a single electrode. In other words, only relative value of electrode potential can be determined by connecting the half cell with some standard electrode as the reference electrode.

(ii) The electrode potential of iron,

(i.e.,  $E^{\circ}_{Fe^{2+}/Fe} = -0.44 \text{ V}$ ) is lower than that of copper (i.e.,  $E^{\circ}_{Cu^{2+}/Cu} = +0.34 \text{ V}$ ) and hence Fe has greater

tendency to get converted into Fe<sup>2+</sup> ions than Cu. In other words, iron undergoes oxidation more readily than copper.

(iii) An electrode with lower electrode potential has more tendency to get oxidised. In other words, it has more tendency to release electrons, and hence acts as a reducing agent.

(iv) Copper ( $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = + 0.34 \text{ V}$ ) has lower electrode potential than silver ( $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$ ). Therefore, Cu releases electrons and gets oxidised to  $\text{Cu}^{2+}$  ions while  $\text{Ag}^{+}$  ions accept these electrons and get reduced to Ag metal.

 $Cu_{(s)} + 2Ag^{+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Ag_{(s)}$ 

The chemical energy of this reaction appears as heat and hence the solution becomes hot. Since, the reverse reaction cannot occur (because the  $E^{\circ}$  of Ag is higher than that of Cu). Therefore, no change is observed.

(v) Fe has lower electrode potential ( $E_{Fe}^{\circ}^{\circ}^{2+}/F_{e}^{\circ} = -0.44 \text{ V}$ ) than that of hydrogen ( $E_{H}^{\circ}^{+}/H_{2}^{\circ} = 0.0 \text{ V}$ ), therefore, Fe is a better reducing agent than  $H_{2}$  and hence reduces  $H^{+}$  ions to produce  $H_{2}$  gas.

 $Fe_{(s)} + 2H^{+}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + H_{2(g)}$ In contrast, Ag has higher electrode potential  $(E^{\circ}_{Ag^{+}/Ag} = + 0.80 \text{ V})$  than hydrogen. Therefore,  $H_{2}$  is a better reducing agent than Ag. In other words, Ag cannot reduce  $H^{+}$  ions to produce  $H_{2}$  gas.

OR

(i) 
$$Zn_{(s)} \longrightarrow Zn_{(aq)}^{2+} + 2e^{-}$$
 (oxidation);  
 $Pb^{2+} \longrightarrow Pb_{++}$  (reduction)

 $Pb^{2+}_{(aq)} + 2e^{-} \longrightarrow Pb_{(s)}$  (reduction) Zn is oxidised to  $Zn^{2+}_{(aq)}$ ,  $Pb^{2+}$  is reduced to Pb;

 $Pb^{2+}$  is the oxidiser and Zn is the reducer.

(ii) 
$$2Fe^{3+} + 2e^{-} \longrightarrow 2Fe^{2+}$$
 (reduction);

$$2I^- \longrightarrow I_2 + 2e^-$$
 (oxidation)

Fe<sup>3+</sup> is reduced to Fe<sup>2+</sup>, I<sup>-</sup> is oxidised to I<sub>2</sub>;

I is the reducer and Fe<sup>3+</sup> is the oxidiser.

(iii) 
$$2Na \longrightarrow 2Na^+ + 2e^-$$
 (oxidation);

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$
 (reduction)

Na is oxidised to Na<sup>+</sup> and Cl<sub>2</sub> is reduced to Cl<sup>-</sup>;

Na is the reducer and Cl<sub>2</sub> is the oxidiser.

(iv) Mg 
$$\longrightarrow$$
 Mg<sup>2+</sup> + 2 $e^-$ (oxidation);

$$Cl_2 + 2e^- \longrightarrow 2Cl^-$$
 (reduction)

Mg is oxidised to Mg<sup>2+</sup> while Cl<sub>2</sub> is reduced to Cl<sup>-</sup>;

Mg is the reducer and  $Cl_2$  is the oxidiser.

(v) 
$$Zn \longrightarrow Zn^{2+} + 2e^-$$
 (oxidation);

$$2H^+ + 2e^- \longrightarrow H_2(reduction)$$

Zn is oxidised to  $Zn^{2+}$  while  $H^{+}$  is reduced to  $H_2$ ; Zn is the reducer and  $H^{+}$  is the oxidiser.

36. (i) (a) From the graph, it is clear that in 1 to 5 h,

$$\Delta[A] = (0.3 - 0.5) \text{ mol } L^{-1} = -0.2 \text{ mol } L^{-1}$$

$$\Delta[B] = (0.6 - 0.2) \text{ mol } L^{-1} = 0.4 \text{ mol } L^{-1}$$

The amount of B formed is double the amount of A consumed. So, in the equation,  $A \rightleftharpoons nB$ ,

At equilibrium, n is 2.

(b) 
$$[A]_{eq} = 0.3 \text{ mol } L^{-1}$$
;  $[B]_{eq} = 0.6 \text{ mol } L^{-1}$ 

$$K_{eq} = \frac{[B]^2}{[A]} = \frac{(0.6 \text{ mol L}^{-1})^2}{0.3 \text{ mol L}^{-1}} = 1.2 \text{ mol L}^{-1}$$

(ii) (a) Liquid NH<sub>3</sub> undergoes self ionisation according to the reaction,  $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$ 

Thus, in liquid ammonia the strongest acid is NH<sup>+</sup><sub>4</sub> and the strongest base is NH<sub>2</sub>.

Thus, all ammonium salts act as acids and amides act as bases in liquid NH<sub>3</sub>.

(b) 
$$CO_{2(g)} + nH_2O_{(l)} \rightleftharpoons CO_{2(aq)}$$

The process occurs with decrease in randomness. Since this reaction is feasible, it must be exothermic in the forward direction. Therefore, the increase of temperature pushes the reaction in the backward direction, thereby decreasing the solubility.

(i)  $1.5 \text{ M Na}_2\text{CO}_3 \text{ gives } [\text{CO}_3^{2-}] = 1.5 \text{ M}$  $K_{sp}$  for  $Ag_2CO_3 = [Ag^+]^2[CO_3^{2-}]$ 

$$\therefore [Ag^{+}] = \sqrt{\frac{K_{sp} \text{ for } Ag_{2}CO_{3}}{[CO_{3}^{2-}]}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}}$$

$$= 2.34 \times 10^{-6} \text{ M}$$

$$K_{sp} \text{ for } AgCl = [Ag^{+}] [Cl^{-}]$$

$$= (2.34 \times 10^{-6}) \left(\frac{0.0026}{35.5}\right) = 1.71 \times 10^{-10}$$

(ii) 
$$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$$

$$K_{sp} = [Pb^{2+}][OH^{-}]^{2} = s \times (2s)^{2} = 4s^{3}$$
$$= 4 \times (6.7 \times 10^{-6})^{3} = 1.20 \times 10^{-15}$$

In a solution with pH = 8,  $[H^+] = 10^{-8}$  and  $[OH]^- = 10^{-6}$ 

$$\therefore 1.20 \times 10^{-15} = [Pb^{2+}] \times (10^{-6})^2$$

or 
$$[Pb^{2+}] = \frac{1.20 \times 10^{-15}}{(10^{-6})^2} = 1.20 \times 10^{-3} \text{ M}$$

37. (i) 
$$N_{2(g)} + 3H_{2(g)} \Longrightarrow 2NH_{3(g)}$$

$$\Delta n = 2 - 4 = -2$$
;  $(T = 400 + 273 \text{ K} = 673 \text{ K})$ 

 $K_p = K_c (RT)^{\Delta n}$ 

$$1.64 \times 10^{-4} \text{ atm}^{-2} = K_c (0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 673 \text{ K})^{-2}$$

or 
$$K_c = \frac{1.64 \times 10^{-4} \text{ atm}^{-2}}{(0.0821 \times 673 \text{ L atm mol}^{-1})^{-2}} = 0.5006 \text{ L}^2 \text{mol}^{-2}$$

Now,  $\Delta G^{\circ} = -2.303 \ RT \log K$ 

If 
$$K = K_p$$
,  $\Delta G^{\circ} = -2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (673 \text{ K}) \times \log(1.64 \times 10^{-4})$ 

= 
$$-2.303 \times 8.314 \times 673 \times (-3.7852)$$
 J mol<sup>-1</sup>

 $= +48.78 \text{ kJ mol}^{-1}$ 

If 
$$K = K_c$$
,

$$\Delta G^{\circ} = -2.303 \times (8.314 \text{ JK}^{-1} \text{ mol}^{-1}) (673 \text{ K}) \times \log(0.5006)$$
  
= -2.303 × 8.314 × 673 × (-0.3005) J mol<sup>-1</sup>  
= 3.87 kJ mol<sup>-1</sup>

(ii) From the relation  $K_p = K_c (RT)^{\Delta n_g}$ , if  $\Delta n_g = 0$ ,  $K_p = K_c$ 

$$e.g., H_2 + I_2 \rightleftharpoons 2HI$$

$$\Delta n_g = (2-2) = 0$$

OR

(i) Pyridine is a weak base. Thus, pyridine + pyridinium chloride solution is a basic buffer. Hence,

$$pOH = pK_b + log [Salt]/[Base]$$

$$\therefore$$
 p $K_b = -\log K_b = -\log(1.5 \times 10^{-9})$ 

$$= 9 - 0.1761 = 8.8239$$

[Pyridine] = 0.20 M (Given),

[Pyridinium chloride] = 
$$\frac{0.15}{500} \times 1000 = 0.30 \text{ M}$$

$$\therefore \quad pOH = 8.8239 + \log \frac{0.30}{0.20} = 8.8239 + 0.1761 = 8.999$$

i.e.,  $-\log[OH^-] = 8.999 \implies [OH^-] = 1.002 \times 10^{-9}$ 

 $[OH^{-}]$  from  $H_2O = 10^{-7}$  M cannot be neglected.

Hence, total  $[OH^{-}] = 1.002 \times 10^{-9} + 10^{-7}$ 

$$=10^{-9}(1.002 + 100) = 101.002 \times 10^{-9} \text{ M} \approx 1.01 \times 10^{-7} \text{ M}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.01 \times 10^{-7}} = 9.9 \times 10^{-8} \text{ M}$$

 $pH = -log(H^+) = -log(9.9 \times 10^{-8}) = 8 - 0.9956 = 7.009$ 

- (ii) On the basis of Le Chatelier's principle in each case,
- (a) Equilibrium will shift in the forward direction.
- (b) Equilibrium will shift in the backward direction.
- (c) Equilibrium will shift in the backward direction.
- (d) Equilibrium will shift in the forward direction



# MONTHLY TEST DRIVE MONTHLY TEST MONTHLY T

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks: 120

#### Hydrogen/The s-Block Elements

Time Taken : 60 Min.

#### NEET # AIIMS

#### **Only One Option Correct Type**

- One mole of magnesium nitride on reacting with an excess of water gives
  - (a) one mole of ammonia
  - (b) two moles of nitric acid
  - (c) two moles of ammonia
  - (d) one mole of nitric acid,
- 2. The bond angle and dipole moment of water respectively are
  - (a) 109.5°, 1.84 D
- (b) 104.5°, 1.56 D
- (c) 104.5°, 1.84 D
- (d) 102.5°, 1.56 D
- An unknown inorganic compound (X) loses its water of crystallisation on heating and its aqueous solution gives the following reactions.
  - (I) It gives a white turbidity with dilute HCl solution.
  - (II) It decolourises a solution of iodine in potassium iodide.
  - (III) It gives a white precipitate with silver nitrate solution which turns black on standing.

The compound (X) is

- (a) Na<sub>2</sub>CO<sub>3</sub>·10H<sub>2</sub>O
- (b)  $Na_2S_2O_3 \cdot 5H_2O$
- (c)  $Na_2SO_4\cdot 10H_2O$
- (d) none of these.
- 4. The solubility of lithium halides in non-polar solvents follows the order
  - (a) LiI > LiBr > LiCl > LiF
  - (b) LiF > LiI > LiBr > LiCl
  - (c) LiCl > LiF > LiI > LiBr
  - (d) LiBr > LiCl > LiF > LiI
- 5. Some statements about heavy water are given below:
  - (i) Heavy water is used as a moderator in nuclear reactors.

- (ii) Heavy water is more associated than ordinary water.
- (iii) Heavy water is more effective solvent than ordinary water.

Which of the above statements are correct?

- (a) (i) and (ii)
- (b) (i), (ii) and (iii)
- (c) (ii) and (iii)
- (d) (i) and (iii)
- Which one of the following sequences represents the increasing order of the polarising power of the cationic species, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Be<sup>2+</sup>
  - (a)  $Ca^{2+} < Mg^{2+} < Be^{2+} < K^{+}$
  - (b)  $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
  - (c)  $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
  - (d)  $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
- 7. BaSO<sub>4</sub> is water insoluble although it is an ionic compound because of
  - (a) low lattice energy
  - (b) high bond energy
  - (c) lattice energy > solvation energy
  - (d) solvation energy > lattice energy.
- 8. A metal M readily forms its sulphate MSO<sub>4</sub> which is water-soluble. It forms its oxide MO which becomes inert on heating. It forms an insoluble hydroxide M(OH)<sub>2</sub> which is soluble in NaOH solution. Then M is
  - (a) Mg
- (b) Ba
- (c) Ca
- (d) Be
- 9. The electron affinity of Be is similar to
  - (a) He
- (b) B
- (c) Li
- (d) Na
- 10. Monovalent sodium and potassium ions, divalent magnesium and calcium ions are found in
  - (a) lipids
- (b) biological fluids
- (c) fats
- (d) enzymes.

11.  $NH_4Cl + (A) \longrightarrow Microcosmic salt$   $\downarrow Heat$   $(B) \xrightarrow{Heat} (C)$   $(A), (B) \text{ and } (C) \text{ are} \qquad Violet bead}$ 

(A), (B) and (C) are

- (a)  $Na_3PO_4$ ,  $NaPO_3$ ,  $Mn_3(PO_4)_2$
- (b)  $Na_2HPO_4$ ,  $Na_3PO_4$ ,  $Mn_3(PO_4)_2$
- (c) Na<sub>2</sub>HPO<sub>4</sub>, NaPO<sub>3</sub>, Mn(PO<sub>3</sub>)<sub>2</sub>
- (d) Na<sub>2</sub>HPO<sub>4</sub>, NaPO<sub>3</sub>, NaMnPO<sub>4</sub>
- 12. Oxidation state of hydrogen is zero in
  - (a) CaH<sub>2</sub>

(b) NaH

(c) PdH<sub>2</sub>

(d) NH<sub>3</sub>

#### Assertion & Reason Type

**Directions**: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.
- 13. Assertion:  $H_2O_2$  is stored in wax-lined glass or plastic vessels.

Reason: H2O2 decomposes slowly on exposure to light.

14. Assertion: Sulphides are oxidised by H<sub>2</sub>O<sub>2</sub> in presence of Fe (III).

Reason: Fe (III) reduces sulphide to sulphate.

15. Assertion: Li<sub>2</sub>CO<sub>3</sub> decomposes easily on heating to form Li<sub>2</sub>O and CO<sub>2</sub>.

Reason: Li<sup>+</sup> is very small in size and applies very high polarising power on  $CO_3^{2-}$  ion leading to the decomposition of Li<sub>2</sub>CO<sub>3</sub>.

#### JEE MAIN / ADVANCED:

#### Only One Option Correct Type

- 16. Read the following statements.
  - I. Cs<sup>+</sup> is highly hydrated.
  - II. Li has highest melting point among Li, Na, K and Rb.
  - III. In alkali metals, only Li forms nitride.

The correct statements are

(a) I and II

(b) II and III

(c) I and III

(d) I, II and III

17. The melting point of most of the solid substances increase with an increases of pressure. However, ice melts at a temperature lower than its usual melting point when pressure is increased. This is because

- (a) ice is less denser than H<sub>2</sub>O
- (b) pressure generates heat
- (c) the chemical bonds break under pressure
- (d) ice is not a true solid.
- 18. Decomposition of  $H_2O_2$  is retarded by
  - (a) H<sub>3</sub>PO<sub>4</sub> (b) alcohol

(c) acetanilide

(d) all of these.

- 19. Identify the correct statement.
  - (a) The percentage of calcium is lower in gypsum in comparison to plaster of Paris.
  - (b) Gypsum is not a natural product. It is obtained by heating of plaster of Paris.
  - (c) Plaster of Paris is obtained by hydration of gypsum.
  - (d) Plaster of Paris is formed by oxidation of gypsum.

#### More than One Options Correct Type

- 20. Select the correct statements about barium.
  - (a) It shows photoelectric effect.
  - (b) It is silvery white metal.
  - (c) It forms Ba(NO<sub>3</sub>)<sub>2</sub> which is used in preparation of green fire.
  - (d) Its ionisation energy is less than radium.
- 21. Highly pure dilute solution of sodium in liquid ammonia
  - (a) shows blue colour
  - (b) exhibits electrical conductivity
  - (c) produces sodium amide
  - (d) produces hydrogen gas.



- 22. When zeolite, which is hydrated sodium aluminium silicate, is treated with hard water the sodium ions are exchanged with

  - (a)  $H^+$  ions (b)  $Ca^{2+}$  ions

  - (c)  $SO_4^{2-}$  ions (d)  $Mg^{2+}$  ions.
- 23. Select the correct statement(s) about limelight.
  - (a) It is produced in oxyhydrogen flame.
  - (b) It is used in welding.
  - (c) Temperature of limelight is sufficient to melt even platinum.
  - (d) It is produced in an endothermic reaction.

#### Numerical Value Type

- 24. To 8.4 mL H<sub>2</sub>O<sub>2</sub>, excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution. Volume strength of H<sub>2</sub>O<sub>2</sub> solution is
- 25. Number of moles of acidified potassium permanganate reduced by five moles of H<sub>2</sub>O<sub>2</sub> is
- 26. Magnesium oxide when mixed with a saturated solution of magnesium chloride sets to a hard mass like cement known as 'sorel cement'. The composition of sorel cement is MgCl<sub>2</sub>·nMgO·xH<sub>2</sub>O. The value of n is

#### Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage:

The chemistry of alkaline earth metals is very much like that of the alkali metals. However, some differences arise because of reduced atomic and ionic sizes and increased cationic charges in case of alkaline earth metals. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. Some important compounds of calcium and sodium includes calcium oxide (lime), calcium sulphate (Plaster of Paris), calcium carbonate (limestone) sodium hydroxide (Caustic soda) and sodium hydrogen carbonate (Baking soda).

	Column-I (Compound)		Column-II (Use)
P.	CaCO <sub>3</sub>	Ι	Used in gun powder
Q.	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	II	Used in fire extinguishers
R.	NaNO <sub>3</sub>	Ш	Used as a flux in metallurgy
S.	NaHCO <sub>3</sub>	IV	Used in black and white photography

- 27. Which of the following has the correct combination considering column I and column II?
  - (a)  $Q \rightarrow IV$
- (b)  $R \rightarrow II$
- (c)  $P \rightarrow I$
- (d)  $S \rightarrow III$
- 28. Which of the following has the correct combination considering column I and column II?
  - (a)  $P \rightarrow IV$
- (b)  $Q \rightarrow I$ 
  - (c)  $R \rightarrow III$
- (d)  $S \rightarrow II$

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage:

Dihydrogen under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called hydrides. If 'E' is the symbol of an element then hydride can be expressed as  $EH_x$  (e.g., MgH<sub>2</sub>) or  $E_mH_n$  (e.g., B<sub>2</sub>H<sub>6</sub>).

	Column-I (Hydride)		Column-II (Type of hydride)			
P.	BeH <sub>2</sub>	I	Complex			
Q.	SiH <sub>4</sub>	II	Interstitial			
R.	LaH <sub>3</sub>	III	Covalent			
S.	LiAlH <sub>4</sub>	IV	Polymeric			

- 29. Which of the following has the correct combination considering column I and column II?
  - (a)  $P \rightarrow II$
- (b)  $Q \rightarrow IV$
- (c)  $R \rightarrow III$
- (d)  $S \rightarrow I$
- 30. Which of the following has the correct combination considering column I and column II?
  - (a)  $P \rightarrow IV$
- (b)  $Q \rightarrow I$
- (c)  $R \rightarrow III$
- (d)  $S \rightarrow II$



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# Class

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#### Only One Option Correct Type

- 1. If rate constant for the first-order decomposition of ethylene oxide into CH4 and CO follows the equation :  $\log k(\text{in s}^{-1}) = 14.34 - (1.25 \times 10^4 \text{ K})/T$ . Then the activation energy of the reaction, the rate constant at 700 K and frequency factor, A will be respectively
  - (a)  $239.3 \text{ kJ mol}^{-1}$ ,  $3.02 \times 10^{-4} \text{ s}^{-1}$ ,  $2.19 \times 10^{14} \text{ s}^{-1}$
  - (b)  $400.12 \text{ kJ mol}^{-1}$ ,  $2.168 \times 10^{-4} \text{ s}^{-1}$ ,  $3.02 \times 10^4 \text{ s}^{-1}$
  - (c)  $339.4 \text{ kJ mol}^{-1}$ ,  $2.02 \times 10^{-10} \text{ s}^{-1}$ ,  $4.50 \times 10^7 \text{ s}^{-1}$
  - (d)  $315.8 \text{ kJ mol}^{-1}$ ,  $3.02 \times 10^{-4} \text{ s}^{-1}$ ,  $3.168 \times 10^{14} \text{ s}^{-1}$ .
- A metal gives two chlorides 'A' and 'B'. 'A' gives black precipitate with NH<sub>4</sub>OH and 'B' gives white. With KI 'B' gives a red precipitate soluble in excess of KI. Here 'A' and 'B' are respectively
  - (a) HgCl<sub>2</sub> and Hg<sub>2</sub>Cl<sub>2</sub> (b) Hg<sub>2</sub>Cl<sub>2</sub>, HgCl<sub>2</sub>
- - (c) HgCl<sub>2</sub> and HgCl
- (d) none of these.
- What will be the equilibrium constant of the cell reaction,  $2Ag^{+} + Zn \rightarrow 2Ag + Zn^{2+}$  occurring in the zinc-silver cell at 25°C when  $[Zn^{2+}] = 0.10 \text{ M}$ and  $[Ag^{\dagger}] = 10 \text{ M}$ ? The EMF of the cell is found to be 1.62 volts.
  - (a)  $5.26 \times 10^{49}$
- (b)  $6.03 \times 10^{51}$
- (c)  $6.26 \times 10^{52}$
- (d)  $8.128 \times 10^{52}$

An organic compound A,  $C_8H_4O_3$ , in dry benzene in the presence of anhydrous AlCl<sub>3</sub> gives compound B. The compound B on treatment with PCl<sub>5</sub>, followed by reaction with H<sub>2</sub>-Pd, BaSO<sub>4</sub> gives compound C, which on reaction with hydrazine gives a cyclised compound D. The compound D is

(a) 
$$C_6H_5$$

(b)  $C_8N$ 
 $C_6H_5$ 
 $C_6H_5$ 

- Ba<sup>2+</sup>, CN<sup>-</sup> and Co<sup>2+</sup> form an ionic complex. If this complex is 75% ionised in aqueous solution with van't Hoff factor (i) equal to four and paramagnetic moment is equal to 1.73 B.M. (due to spin only) then, the hybridisation state of Co(II) in the complex will be

  - (a)  $sp^3d$  (b)  $d^2sp^3$  (c)  $sp^3d^2$  (d)  $dsp^3$

- 6. Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?
  - (a) CO<sub>2</sub> is more volatile than CS<sub>2</sub>.
  - (b) Metal sulphides are thermodynamically more stable than CS<sub>2</sub>.
  - (c) CO<sub>2</sub> is thermodynamically more stable than CS<sub>2</sub>.
  - (d) Metal sulphides are less stable than the corresponding oxides.
- 7. A tripeptide is written as Glycine-Alanine-Glycine. The correct structure of the tripeptide is

8. Identify (X) and (Y) in the following reaction sequence.

CH<sub>1</sub>

sequence.

H<sub>1</sub>C

OH

$$\xrightarrow{H^{+}}$$
 $(X)$ 
 $\xrightarrow{Q_{1}}$ 
 $(X)$ 
 $(X)$ 

- 9. Which one of the following statements is not true?
  - (a) Buna-S is a copolymer of butadiene and styrene.
  - (b) Natural rubber is a 1,4-polymer of isoprene.
  - (c) In vulcanization, the formation of sulphur bridges between different chains make rubber harder and stronger.
  - (d) Natural rubber has the *trans*-configuration at every double bond.
- 10. Iron (II) oxide, FeO, crystal has a cubic structure and each edge of the unit cell is 5.0 Å. If the density of the oxide is 4.0 g cm<sup>-3</sup>, then what will be the number of Fe<sup>2+</sup> ions present in each unit cell?
  - (a) 3
- (b) 2
- (c) 4
- (d) 6

#### More Than One Options Correct Type

- 11. 1.2575 g sample of [Cr(NH<sub>3</sub>)<sub>6</sub>]SO<sub>4</sub>Cl (Mol. wt. = 251.5) is dissolved to prepare 250 mL solution showing an osmotic pressure of 1.478 atm at 27°C. Which of the following statements is/are correct about this solution?
  - (a) Given complex furnishes three ions in solution.
  - (b) The van't Hoff factor is 3.
  - (c) The equilibrium molarity of  $[Cr(NH_3)_6] SO_4Cl = 0$ .
  - (d) The equilibrium molarity of  $[Cr(NH_3)_6]^{3+}$ = 0.02 M.
- 12. Nitrogen(I) oxide is produced by
  - (a) thermal decomposition of ammonium nitrate
  - (b) disproportionation of N<sub>2</sub>O<sub>4</sub>
  - (c) thermal decomposition of ammonium nitrite
  - (d) interaction of hydroxylamine and nitrous acid.
- 13. Which of the following is/are examples of Sandmeyer's reaction?
  - (a)  $C_6H_5N_2Cl^{-} \xrightarrow{CuCl} C_6H_5Cl$
  - (b)  $C_6H_5N_2Cl^{-}\xrightarrow{CuBr}C_6H_5Br$
  - (c)  $C_6H_5N_2Cl^{-}\xrightarrow{CuCN}C_6H_5CN$
  - (d)  $C_6H_5\overset{+}{N}_2Cl^-\xrightarrow{KCN}C_6H_5I$

14. Which of the following is correct option for the given reaction sequence?

OH

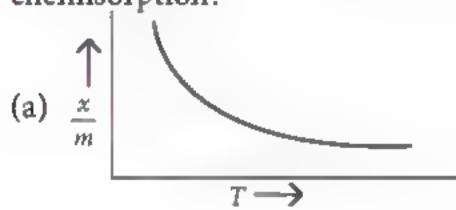
NaOH (1 eq.)

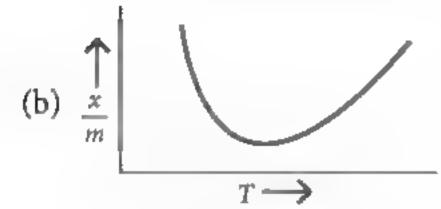
$$P$$
 $C1$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $CH_2$ 
 $OH$ 
 $OH$ 

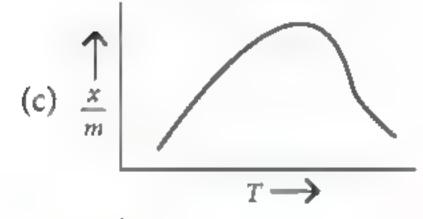
(a) 
$$R - \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc \bigcirc$$

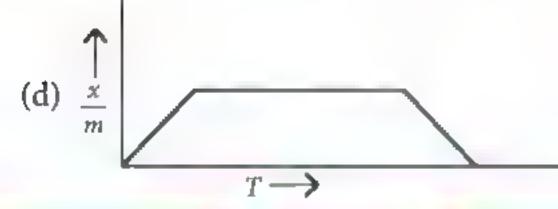
(d) 
$$P = \bigcirc^{OH}$$

15. Which is not the adsorption isobar for chemisorption?









#### SOLUTIONS

1. (a): Arrhenius equation,  $k = Ae^{-E_a/RT}$ or  $\log k = \log A - E_a/(2.303 RT)$  ...(i) Also,  $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T (given)}$  ...(ii) Now, from eqs. (i) and (ii),  $E_a/2.303 RT = 1.25 \times 10^4 \text{ K/T}$ 

- .. Activation energy,  $E_a = (1.25 \times 10^4 \text{ K}) (2.303)$   $(8.314 \text{ J K}^{-1} \text{ mol}^{-1})$   $= 23.93 \times 10^4 \text{ J mol}^{-1} = 239.3 \text{ kJ mol}^{-1}$ At T = 700 K:  $\log k = 14.34 - (1.25 \times 10^4 \text{ K}/700 \text{ K})$ = -3.52
- $\therefore$  Rate constant,  $k = 3.02 \times 10^{-4} \text{ s}^{-1}$ It is evident from Eqs. (i) and (ii) that  $\log A = 14.34$
- $\therefore$  Frequency factor,  $A = 2.19 \times 10^{14} \text{ s}^{-1}$
- 2. (b): 'A' is  $Hg_2Cl_2$  and 'B' is  $HgCl_2$ .  $Hg_2Cl_2 + 2NH_4OH \longrightarrow$ (A)  $Hg \stackrel{NH_2}{\longleftarrow} + Hg + NH_4Cl + 2H_2O$

HgCl<sub>2</sub> + 2NH<sub>4</sub>OH 
$$\longrightarrow$$
 Hg $\stackrel{NH_2}{\longleftarrow}$  + NH<sub>4</sub>Cl + 2H<sub>2</sub>O

White ppt.

$$HgCl_2 + 2KI \longrightarrow HgI_2 + 2KCl$$
 $(B)$ 
 $Red ppt.$ 
 $HgI_2 + 2KI \longrightarrow K_2HgI_4$ 
 $(Excess)$ 
 $Nessler's reagent$ 
 $(Soluble)$ 

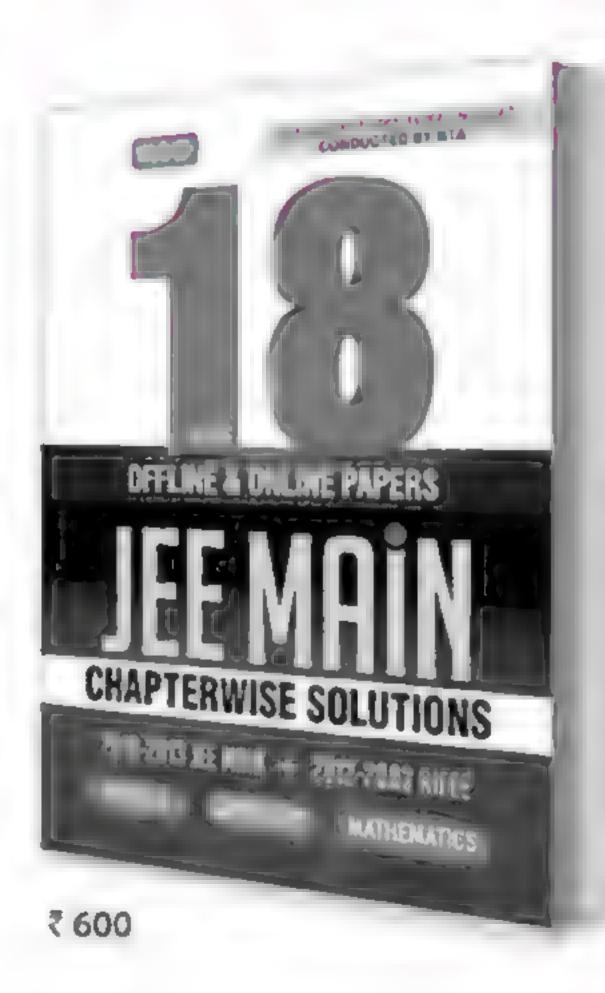
3. (b): For the cell,  $2Ag^{+} + Zn \rightarrow 2Ag + Zn^{2+} (n = 2)$   $E = E^{\circ} - \frac{0.0591}{n} \log K_{c}$   $1.62 = E^{\circ} - \frac{0.0591}{2} \log \frac{0.01}{10}$  $E^{\circ} = 1.62 - 0.089 = 1.53 \text{ volt}$ 

$$E^{\circ} = \frac{0.0591}{n} \log K_{\text{eq}} \implies 1.53 = \frac{0.0591}{2} \log K_{\text{eq}}$$
  
 $\therefore K_{\text{eq.}} = 10^{51.78} = 6.03 \times 10^{51}$ 

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5. (d): As 
$$\mu = \sqrt{n(n+2)}$$
 B.M.  
 $1.73 = \sqrt{n(n+2)}$ 

 $\therefore$  n=1

One unpaired electron indicates paramagnetic moment.

6. (a): The reduction process is based on the thermodynamic stability of the products and not on their volatility.

9. (d): Natural rubber is cis-1,4 polyisoprene and has only cis-configuration about the double bond.

10. (c) : Volume of the unit cell = 
$$(5 \times 10^{-8} \text{ cm})^3$$
  
=  $1.25 \times 10^{-22} \text{ cm}^3$ 

Density of FeO =  $4.0 \text{ g cm}^{-3}$ 

.. Mass of the unit cell =  $1.25 \times 10^{-22} \text{ cm}^3 \times 4.0 \text{ g cm}^{-3} = 5.0 \times 10^{-22} \text{ g}$  Mass of one molecule of FeO

$$= \frac{\text{Molar mass in gram}}{\text{Avogadro's number}} = \frac{72 \text{ g mol}^{-1}}{6.022 \times 10^{23} \text{ mol}^{-1}}$$
$$= 1.195 \times 10^{-22} \text{ g}$$

.. Number of FeO molecules per unit cell

$$= \frac{5.0 \times 10^{-22} \,\mathrm{g}}{1.195 \times 10^{-22} \,\mathrm{g}} = 4.18 \approx 4$$

Thus, there are four Fe<sup>2+</sup> ions and four O<sup>2-</sup> ions in each unit cell.

11. (a, b, c, d): Molarity = 
$$\frac{w \times 1000}{M \times V_{\text{(mL)}}} = \frac{1.2575 \times 1000}{251.5 \times 250}$$
  
= 0.02 M  
 $\pi = CRT$ 

 $\therefore$   $\pi_{cal} = 0.02 \times 0.0821 \times 300 = 0.4926$  atm

$$\frac{\pi_{\text{obs}}}{\pi_{\text{cal}}} = i = \frac{1.478}{0.4926} = 3$$

As the given complex is dissociated as,

[Cr(NH<sub>3</sub>)<sub>6</sub>]SO<sub>4</sub>Cl 
$$\rightleftharpoons$$
 [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> + SO<sub>4</sub><sup>2-</sup> + Cl<sup>-</sup>
0.02 0 0 0

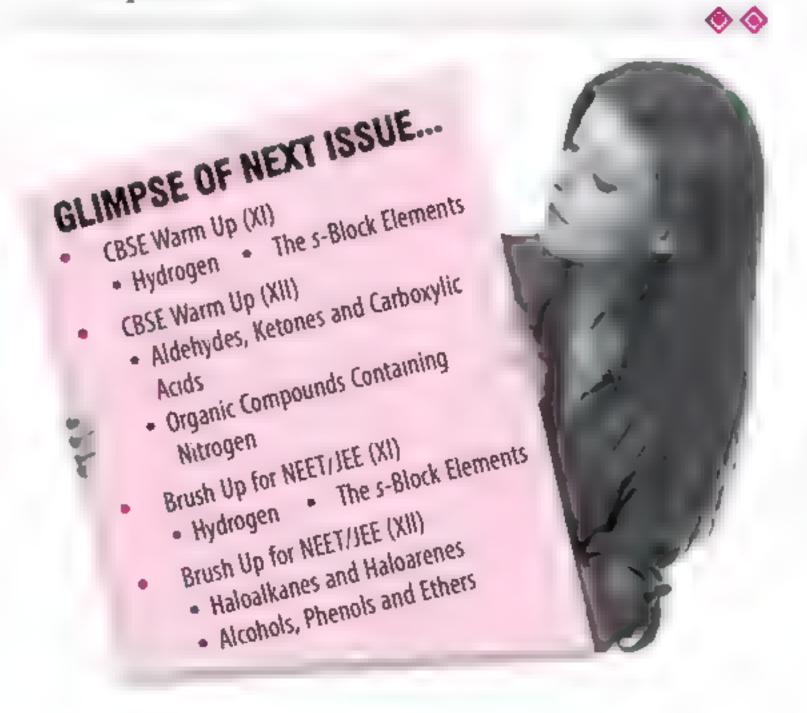
Eq. conc. 0 0.02 0.02

 $\therefore n = 3$ 
 $\therefore \alpha = \frac{i-1}{n-1}$ ;  $\alpha = 1$ 

12. (a, d): 
$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$$
  
 $NH_2OH + HNO_2 \longrightarrow N_2O + 2H_2O$ 

13. (a, b, c) 14. (a, c, d)

15. (a, b, d): In chemisorption, adsorption first increases and then decreases with increase in temperature.





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2020



#### The d- and f-Block Elements | Coordination Compounds

#### The d- and f-Block Elements

#### THE TRANSITION ELEMENTS (d-BLOCK)

- The elements that lie in between s-block and p-block elements are called transition elements as they show transitional properties between s- and p-block elements.
- d-Block elements in their ground state or in most
- common oxidation state have partially filled d-orbitals. General electronic configuration of d-block elements is  $(n-1)d^{1-10} ns^{0-2}$ .
- It is obvious from the electronic configuration that in transition elements valence electrons are present in outermost shell (ns) as well as in (n − 1) d-orbital i.e., penultimate (last but one) shell.

#### Classification and Electronic Configuration of d-Block Elements

First (3d) Transition Series (Sc - Zn)

At. No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E.C.	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

Second (4d) Transition Series (Y - Cd)

At. No.	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd
E.C.	$4d^1 5s^2$	$4d^25s^2$	$4d^4 5s^1$	$4d^5 5s^1$	$4d^5 5s^2$	$4d^7 5s^1$	$4d^8  5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

<sup>\*</sup>Technetium (Tc) is a synthetic transition metal.

• Third (5d) Transition Series (La-Hg)

At. No.	57	72	73	74	75	76	77	78	79	80
Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
E.C.	$5d^1 6s^2$	$5d^2 6s^2$	$5d^3 6s^2$	$5d^4 6s^2$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	5d <sup>9</sup> 6s <sup>1</sup>	$5d^{10} 6s^1$	$5d^{10} 6s^2$

Fourth (6d) Transition Series (Ac - Cn)

At. No.	89	104	105	106	107	108	109	110	111	112
Element	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
E.C.	$6d^1 7s^2$	$6d^2 7s^2$	$6d^3 7s^2$	$6d^4 7s^2$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$	$6d^{10} 7s^1$	$6d^{10} 7s^2$

#### GENERAL CHARACTERISTICS

Melting and boiling points	High due to strong metallic bonding.			
Enthalpies of atomisation	High due to strong interatomic interactions.			
Oxidation states	Variable due to participation of $ns$ and $(n-1)d$ electrons.			
Metallic Character	Except mercury, all transition elements have typical metallic structure and show all the properties of metals.			
Complex formation	Form complexes due to high nuclear charge and small size and availability of empty $d$ -orbitals to accept lone pair of electrons donated by ligands.			
Coloured compounds	Mostly form coloured compounds due to d-d transitions.			
Magnetic properties	Transition metal ions and their compounds are generally paramagnetic due to presence of unpaired electrons in the $(n-1)d$ -orbitals and it is calculated by using the formula, $\mu = \sqrt{n(n+2)}$ where, $n$ is the no. of unpaired electrons.			
Catalytic behaviour	Due to variable oxidation states and ability to form complexes.			
Interstitial compounds	Due to empty spaces in their lattices, small atoms can be easily accommodated.			
Alloy formation	Due to similar atomic sizes.			

in Ionisation Energy to ineffective shielding of nuclear charge by delectrons which tend to

attract the outer electron

cloud with greater force.

Atomic size Increases slowly due: Decreases slowly in the series upto the First increase, middle due to ineffective shielding of rise to maximum d-electrons and increased nuclear charge! then decrease but at the end of the series there is a slight! because number of increase in atomic radii due to increased unpaired electrons electron-electron repulsion between added first increase then electrons in the same orbital.

M.Pt. and B.Pt. decrease.

Density ::Increases along a series because atomic size decreases whereas atomic mass increases.

#### Electrode potential (E°)

- $E^{\circ}(M^{n+}/M)$  is governed by three factors:
  - Heat of sublimation
  - Heat of ionisation
  - Heat of hydration

For the 3*d*-transition metals the  $E^{\circ}(M^{2+}/M)$  values (in volts) are:

Ti V Cr Mn Fe Co Ni Cu -1.63 - 1.18 - 0.91 - 1.18 - 0.44 - 0.28 - 0.25 + 0.34 - 0.76

The irregular trend is due to variation in ionisation energies and sublimation energies. Except copper, 3d-elements are good reducing agents but weaker than s-block elements.

#### SOME IMPORTANT COMPOUNDS OF TRANSITION ELEMENTS

#### Potassium Dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)

Preparation: It is prepared from chromite ore or ferrochrome (FeCr<sub>2</sub>O<sub>4</sub>).

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$
$$2Na_2CrO_4 + H_2SO_4 \text{ (conc.)} \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

 $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$ 

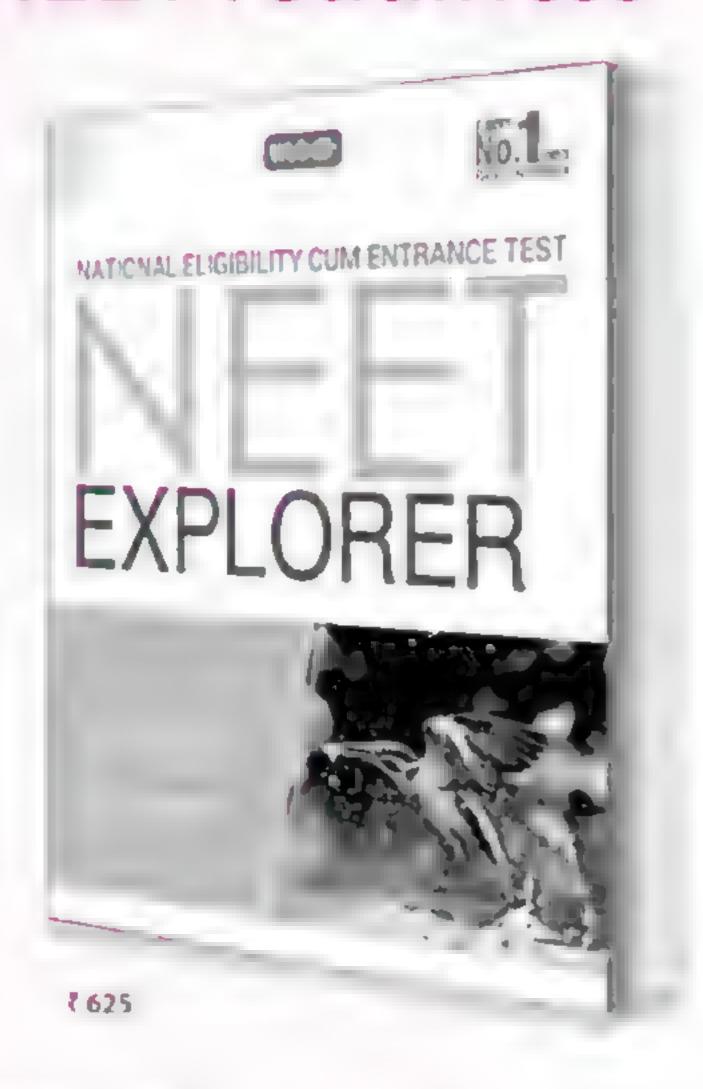
Properties:

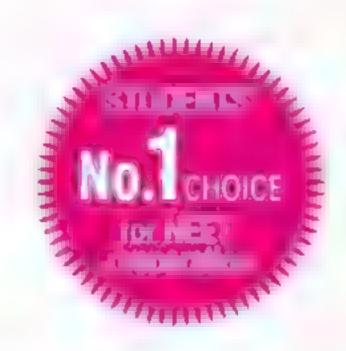
 $K_2Cr_2O_7$  is soluble in hot water.

It is in the form of orange crystals which melt at 400 °C.



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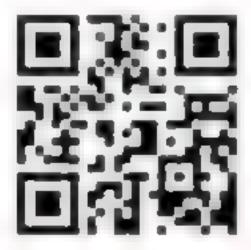


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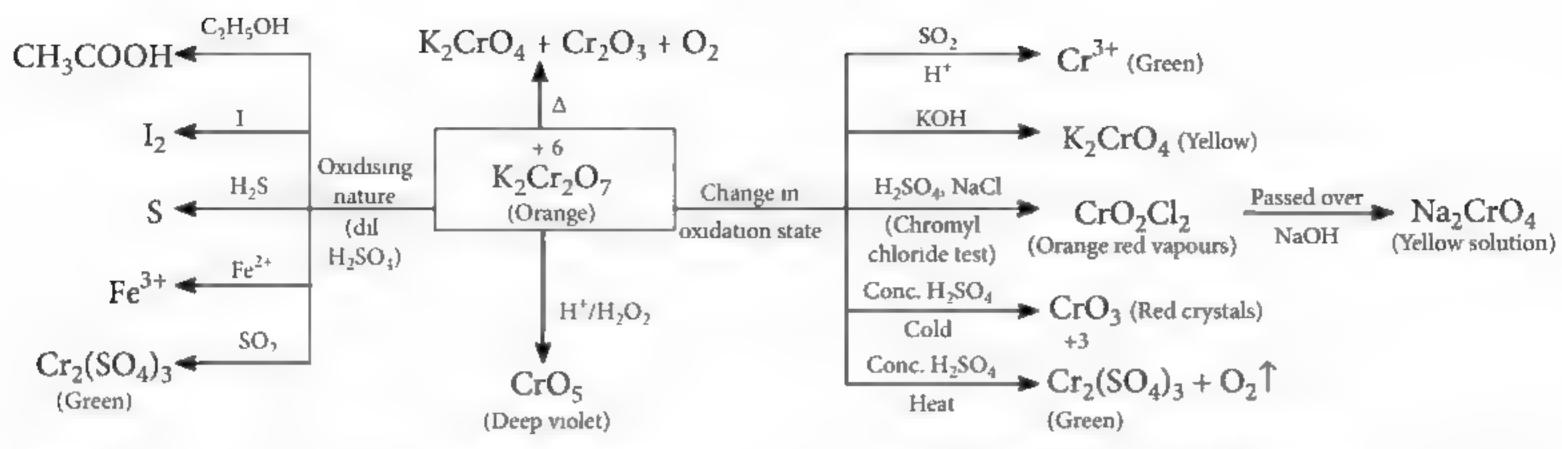
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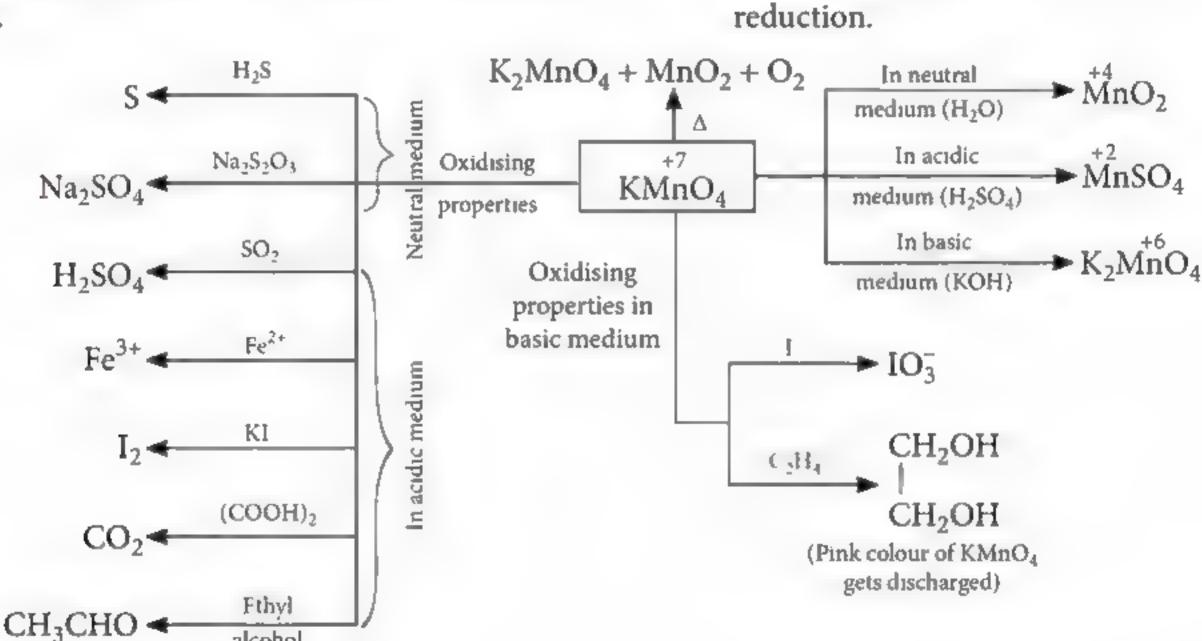


#### Uses:

- In photography, in hardening gelating film.
- In volumetric analysis for estimation of iron and iodine in redox titrations.
- In chrome tanning in leather industry.

#### Potassium Permanganate (KMnO<sub>4</sub>)

Preparation: It is obtained from mineral pyrolusite (MnO<sub>2</sub>).



#### Uses:

- As strong oxidising agent.
- It is used for bleaching of wool, silk and other textile fibres.

alcohol

- As a disinfectant and germicide.
- Alkaline KMnO<sub>4</sub> (Baeyer's reagent) is used for detecting unsaturation in a compound.

#### PEEP LATO PARVIOUS YEARS

1. When neutral or faintly alkaline KMnO<sub>4</sub> is treated with potassium iodide, iodide ion is converted into 'X'. 'X' is

(d) IO<sup>-</sup> (a)  $I_2$ (b) IO<sub>4</sub> (c)  $IO_3^-$ (Odisha NEET 2019)

 $2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$ 

It is fairly soluble in hot water, but sparingly

It exists in the form of deep purple crystals

which become dull in air due to superficial

 $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$ 

soluble in cold water.

Properties:

- The correct option(s) to distinguish nitrate salts of Mn<sup>2+</sup> and Cu<sup>2+</sup> taken separately is (are)
  - (a) Mn<sup>2+</sup> shows the characteristic green colour in the flame test
  - (b) only Cu<sup>2+</sup> shows the formation of precipitate by passing H<sub>2</sub>S in acidic medium
  - (c) only Mn<sup>2+</sup> shows the formation of precipitate by passing H<sub>2</sub>S in faintly basic medium
  - (d) Cu2+/Cu has higher reduction potential than Mn<sup>2+</sup>/Mn (measured under similar conditions). (JEE Advanced 2018)

- 3. Which of the following ions does not liberate hydrogen gas on reaction with dilute acids?
  - (a) Mn<sup>2+</sup>

(b) Ti<sup>2+</sup>

(c)  $V^{2+}$ 

(d) Cr2+

(JEE Main Online 2017)

#### THE INNER-TRANSITION ELEMENTS (f-BLOCK)

- Lanthanoids: Last electron enters one of the 4f-orbitals. Cerium (at. no. 58) to lutetium (at. no. 71).
- Actinoids: Last electron enters one of the 5*f*-orbitals. Thorium (at. no. 90) to lawrencium (at. no. 103).
- General electronic configuration :  $(n-2)f^{1-14}$  $(n-1)d^{0-1}ns^2$

#### **General Characteristics of Lanthanoids**

Atomic and ionic radii	Decrease steadily on going from La to Lu.
Oxidation states	Most common oxidation state of lanthanoids is +3. Some elements exhibit +2 and +4 oxidation states due to extra stability of empty, half-filled or fully-filled f-subshell. e.g., cerium exhibits +4 oxidation state and Sm, Eu and Yb enhibit +2 oxidation state. Each lanthanoid has a tendency to acquire +3 O.S. Thus, Ce <sup>4+</sup> acts as an oxidising agent and Eu <sup>2+</sup> , Yb <sup>2+</sup> act as strong reducing agents.
Action of air	All the lanthanoids are silvery white soft metals and tarnish readily in moist air. They burn in oxygen of air and form oxides (Ln <sub>2</sub> O <sub>3</sub> type).
Coloured ions	They form coloured ions due to $f$ - $f$ transitions of unpaired electrons. La <sup>3+</sup> and Lu <sup>3+</sup> are colourless ions due to empty $(4f^0)$ or fully-filled $(4f^{14})$ orbitals.
Magnetic properties	La <sup>3+</sup> , Lu <sup>3+</sup> are diamagnetic while trivalent ions of the rest of lanthanoids are paramagnetic.
Reducing They readily lose electrons as good reducing agents.	
Electropositive character	Highly electropositive because of low transition energies.

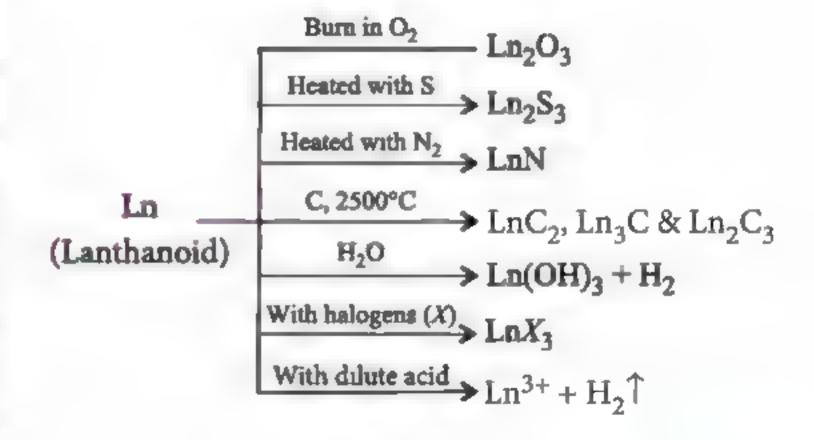
Alloy formation	They form alloys easily with other metals especially iron.			
Tendency to form complexes	Lanthanoids do not have much tendency to form complexes due to low charge density because of their large size. The tendency to form complexes and their stability increases with increasing atomic number.			

- Atomic and ionic radii (Lanthanoid contraction): In lanthanides there is a regular decrease in atomic radii and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as lanthanoid contraction.
  - Causes: In lanthanoids, the nuclear charge increases by one unit at each successive element and a new electron enters the 4f-electron by other electrons from the nuclear attraction, the size of lanthanoid atoms keep on decreasing from La to Lu. Although decrease in atomic radii is not very regular but ionic radii decreases steadily from La to Lu.

#### Consequences of lanthanoid contraction :

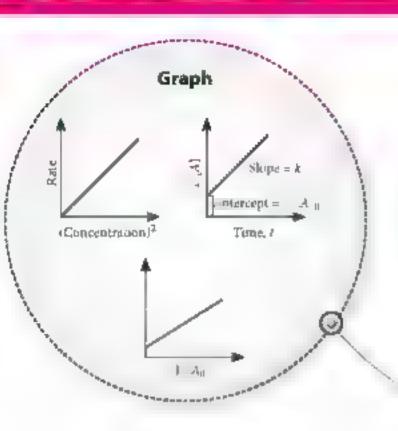
- There is decrease in basic strength of oxides and hydroxides with decrease in the size from La to Lu.
- Similar chemical properties.
- The electronegativity of trivalent ions increases slightly from La to Lu.
- There is small increase in standard electrode potential values from La to Lu.

#### **Chemical Reactivity**



# CONCEPT MAP

### INTEGRATED RATE EQUATIONS (CHEMICAL KINETICS)



#### Half Life

$$t_{1/2} \propto \frac{1}{|A|_0} \Longrightarrow t_{1/2} = \frac{1}{k_1 |A|_0}$$

No. of	Conc. of	Conc. of
half life	reactants	products
L	$[A_0]/2$ (50%)	[A <sub>0</sub> ]/2 (50%)
2	$[A_0]/3 (33.3\%)$	2[A <sub>0</sub> ]/3 (66.66%)
3	$ A_6 /4$ (25%)	3[A <sub>0</sub> ]/4 (75%)
4	[A <sub>0</sub> ]/5 (20%)	4[A <sub>0</sub> ]/5 (80%)

- Rate =  $\frac{d|A|}{dt} = k|A|^0 = k$ 
  - $\bullet = k = \frac{1}{i} \{ [A]_0 [A] \}$

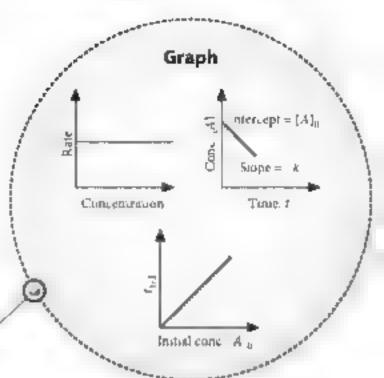
 The concentration of the reactant decreases linearly with time.

$$[A]_t = [A]_0 - kt$$

Unit of k is mol L<sup>-1</sup> time <sup>1</sup>

#### Half Life

 $(t_{1/2})_{\text{zero order}} \approx [A]_0$  (unitial concentration)



#### **Features**

- Rate = k[A]<sup>2</sup> or k [A, [B,
- I A , = Kl + I A]....
- · When concentrations are same

$$k = \frac{1}{t} \frac{x}{n \cdot n - x}$$

 $k = \frac{1}{t} \frac{x}{n + \tau}$ • When concentrations are different

$$k = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

The change in the unit of concentration changes the value of & here.

 Unit of k is L mol time

#### Features

- Rate = & A <sup>4</sup> or k,  $A = [B - C]^*$
- $\frac{1}{[A]_{i}^{2}} \cdot 2kt + \frac{1}{[A]_{i}^{2}}$

When concentrations are same

- $= -k = \frac{1}{t} \frac{x(2a x)}{2a^2(a x)^2}$
- The change in the unit of concentration changes the value of k here
  - Unit of k is: L' moi " time

#### Zero Order Reaction

Second Order Reaction

**Integrated Rate** Equations

> Third Order

(For different order of reaction)

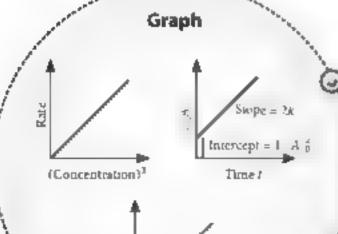
#### Order Reaction Reaction

• Rate =  $-\frac{d[A]}{dt}$  = k,A]<sup>1</sup>

**Features** 

- $ln{A}_t = -kt + ln{A}$
- $k = \frac{2.303}{t_2 t_1} \log_{10} \frac{a x_1}{a x_2}$
- $t = \frac{2.303}{k} \log_{10} \frac{r_0 r_m}{r_c r}$
- Unit of k is time.
- Rate of radioactive decay or disantegration  $N = N_0 e^{-ht}$

$$k = \frac{2.303}{t} \log \frac{\lambda_{in}}{N}$$



$$\frac{3}{2k_3 A_{10}^2}$$

#### **Features** • Rate = k[A]

$$k = \frac{1}{l(n-1)} \begin{bmatrix} 1 & 1 \\ (a-x)^{n-1} & \frac{1}{a^{n-1}} \end{bmatrix}$$
where  $n \ge 2$ 

· Unit of k is mol<sup>1-a</sup> L<sup>a-1</sup> time

#### Half Life

 $\frac{2^{n-s}-1}{k_n(n-1)[A]_0^{n-1}}$ where  $n \ge 2$ 

 $\Rightarrow t_{\perp}, = \frac{1}{(A_{10})^{n-1}}$ 

First

Order

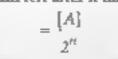
Reaction

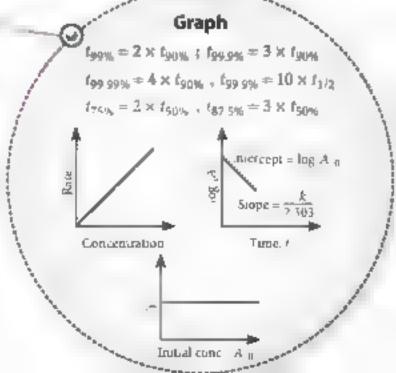
⇒ Independent of the initial concentration.

Half Life

No. of	Conc. of	Conc. of products
half life	reactants	
1	$[A_0]/2 (50\%)$	[A <sub>0</sub> ]/2 (50%)
2	[A <sub>0</sub> ]/4 (25%)	3[A <sub>0</sub> ]/4 (75%)
3	$ A_0 /8$ (12.5%)	7[A <sub>0</sub> ]/8 (87 5%)
4	$[A_0]/16$ (6.25%)	15[A <sub>0</sub> ]/16 (93.75%)

Amount left after n half lives

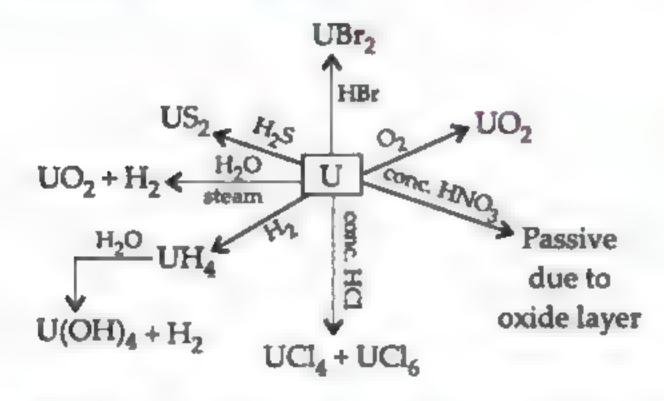




#### **General Characteristics of Actinoids**

Ionic radii	Like lanthanoids, ionic radii decrease regularly across the series. Actinoid contraction is greater due to poor sheilding effect of the 5f-electrons. Further, 5f-orbitals extend in space beyond 6s and 6p-orbitals whereas 4f-orbitals are buried deep.			
Oxidation states	Like lanthanoids, most common oxidation state is $+3$ . They also show oxidation state of $+4$ , $+5$ , $+6$ and $+7$ , e.g., in Th, Pa, U and Np respectively. They show a large number of oxidation states because of very small energy gap between $5f$ , $6d$ and $7s$ subshells.			
Action of air, alkalies and acids	Like lanthanoids they are also silvery white metals, tarnish rapidly in air forming oxide coating and are not attacked by alkalies and are less reactive towards acids.			
Coloured ions	Coloured due to $f$ - $f$ transition except $Ac^{3+}(5f^0)$ , $Cm^{3+}(5f^7)$ and $Th^{4+}(5f^0)$ which are colourless.			
Magnetic properties	They are strongly paramagnetic.			
Density	All actinoids except thorium and americium have high densities.			
Melting and boiling points	High melting and boiling points however there is no regular trend with rise in atomic number.			
Ionisation energy	They have low ionisation energies.			
Reducing agents	All actinoids are strong reducing agents.			
Electropositive	Highly electropositive metals.			
character				

#### **Chemical Reactivity**



# Differences between Lanthanoids and Actinoids

	Lanthanoids	Actinoids			
1.	oxidation states in few	They show higher oxidation states of +4, +5, +6 and +7 besides +3.			
2.		All actinoids are			
3.	They do not form oxo- ions.	They form oxo-ions like $UO_2^{2+}$ , $PuO_2^{2+}$ , $UO_2^{+}$ , etc.			
4.	The compounds of lanthanoids are less basic.	Actinoid compounds are more basic.			

5. They have less tendency They have greater of complex formation. tendency of complex formation.

#### PEER INTO PREVIOUS YEARS.

- 4. The lanthanide ion that would show colour is

  (a) Lu<sup>3+</sup> (b) Sm<sup>3+</sup> (c) La<sup>3+</sup> (d) Gd<sup>3+</sup>

  (JEE Main 2019)
- 5. The reason for greater range of oxidation states in actinoids is attributed to
  - (a) actinoid contraction
  - (b) 5f, 6d and 7s levels having comparable energies
  - (c) 4f and 5d levels being close in energies
  - (d) the radioactive nature of actinoids.

(NEET 2017)

- 6. Which one of the following statements related to lanthanons is incorrect?
  - (a) Europium shows +2 oxidation state.
  - (b) The basicity decreases as the ionic radius decreases from Pr to Lu.
  - (c) All the lanthanons are much more reactive than aluminium.
  - (d) Ce (+) solutions are widely used as oxidizing agent in volumetric analysis.

(NEET Phase II 2016)

#### Pours Foi Extra Scount

- Anhydrous FeSO<sub>4</sub> and CuSO<sub>4</sub> are white because of absence of ligand which causes crystal field splitting, though they have unpaired electrons.
- $\sim$  Cu<sup>2+</sup>(3d<sup>9</sup>,  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = 0.34\text{V}$ ) is more stable than  $Cu^{+}(3d^{10}, E^{\circ}_{Cu^{+}/Cu} = 0.54V)$  except for the cases of large anions, e.g., CuI is more stable than CuI<sub>2</sub>, CuCN is more stable than  $Cu(CN)_2$ .
- (n-1) d-subshell is filled before ns subshell but when cations are formed, electrons are removed from outermost s-subshell instead of penultimate d-subshell.
- Only Os and Ru show +8 oxidation states in their compounds.

- In the oxidation reactions of KMnO<sub>4</sub> in acidic medium, only H<sub>2</sub>SO<sub>4</sub> is used to produce acidic medium and not HCl or HNO3 because HCl reacts with KMnO<sub>4</sub> and produces Cl<sub>2</sub> while HNO<sub>3</sub> itself acts as oxidising agent.
- When the trivalent ion Ln3+ is formed, then screening power of 4f-electrons is no longer equal to unity (but 0.85 since 4f is now penultimate shell and each time an electron is added to 4f orbitals), the nuclear charge increases by 0.15 and thus io nic size decreases continuously from Ce<sup>3+</sup> to Lu<sup>3+</sup>.
- Due to lanthanide contraction, the elements of 5d and 4d-transition series resemble each other much more closely than the elements of 4d and 3d-series.

#### **Coordination Compounds**

#### Addition Compounds

These are the compounds formed by combination of two or more simple compounds are called addition compounds. They are of two types:

Double salt: A compound formed by combination of two or more simple compounds, which is stable in solid state only is called double salt. In solution it breaks into component ions.

e.g.,  $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ;  $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6H_2O;$ KCl-MgCl<sub>2</sub>·6H<sub>2</sub>O;

Potash alum Mohr's salt Carnallite

Complex compound: A compound formed by combination of two or more simple compounds which retain its identity in solid and solution states both is called complex/coordination compound. e.g., K<sub>4</sub>[Fe(CN)<sub>6</sub>] Potassium ferrocyanide [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> Cuprammine sulphate

#### Differences between double salt and coordination compound:

#### **Double Salt**

- constituent species in their aqueous solution.
- 2. They lose their identity in dissolved state.
- 3. In double salts' the metal atoms/ions exhibit their normal valency.
- 4. Their properties are essentially the same as those 4. of their constituent species. For examples, potash alum shows properties of K<sup>+</sup>, Al<sup>3+</sup> etc.

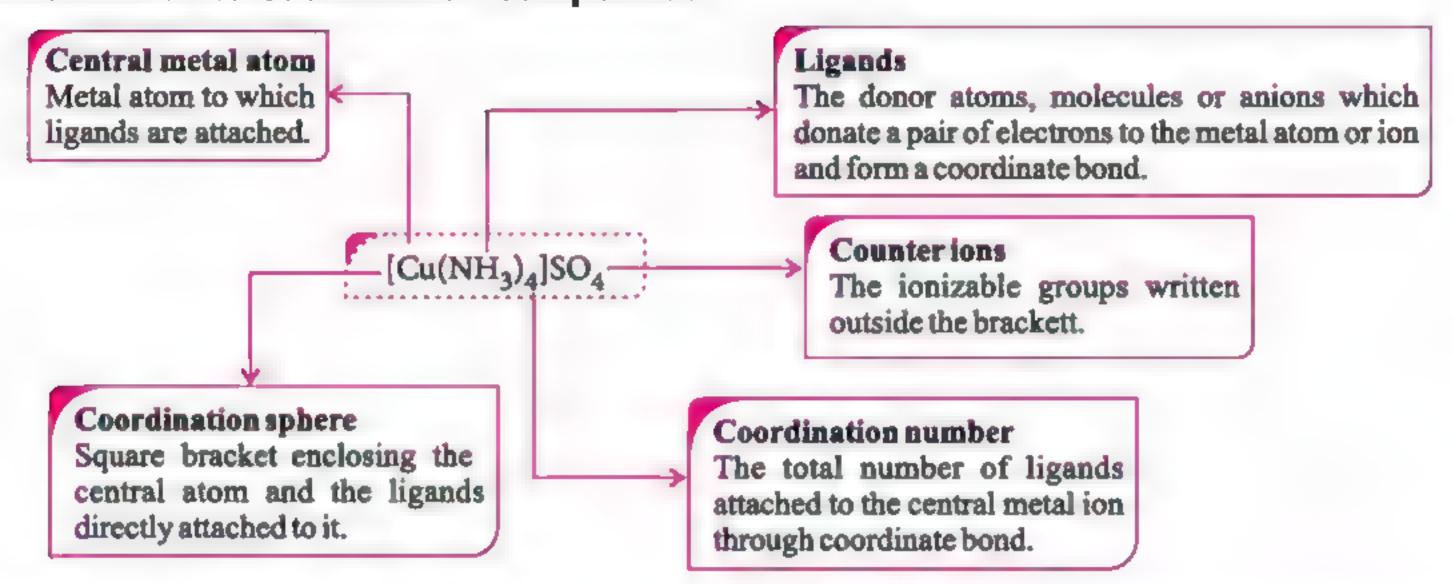
#### Werner's Theory of Coordination Compounds

- According to this theory central metal atom shows two type of linkages (valencies) in coordination compounds.
- Primary valency: Ionisable, corresponds to oxidation state of the central metal atom/ion,

#### **Coordination Compound**

- 1. These exist only in solid state and dissociate into 1. They exist in the solid state as well as in aqueous solution this is because even in the solution, the complex ion does not dissociate into ions.
  - 2. They do not lose their identity in dissolved state.
  - In coordination compounds, the metal ion satisfies its two types of valencies called primary and secondary valencies.
  - Their properties are different from those of their constituents. For example,  $K_4[Fe(CN)_6]$  does not show the test of Fe<sup>2+</sup> and CN<sup>-</sup> ions.
    - satisfied by negative ions, non-directional.
  - Secondary valency: Non-ionisable, corresponds to coordination number of the central metal atom/ ion, satisfied by neutral molecules or ligands, fixed for a metal, directional, giving definite geometry to the complex.

#### **Terms Related to Coordination Compounds**



Ligands

Chelating ligand: When a polydentate ligand coordinates to a metal ion through more than one electron pairs of donor site simultaneously, is called chelation. The resulting complex has ring like structure and such ligand is called chelating ligand. Chelating ligands form more stable complexes than similar ordinary complexes, in which the ligands act as monodentate.

Ambidentate Ligand: A unidentate ligand which can coordinate through two different atoms. e.g., NO<sub>2</sub>, SCN<sup>-</sup>, etc.

Mono or unidentate ligands: Ligands with one donor site. e.g., F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, H<sub>2</sub>O, CN<sup>-</sup>, NO<sub>2</sub>, OH<sup>-</sup>, CO, etc.

Bidentate ligands: Ligands which have two donor atoms at two positions. e.g., Ethylenediammine ( $NH_2CH_2CH_2NH_2$ ),  $NH_2$  oxalate ( $C_2O_4^{2-}$ ), glycinate  $CH_3$  , etc.

Polydentate ligands: The ligands having several donor atoms are called polydentate ligands.

e.g., Diethylenetriammine having 3 donor atoms is tridentate, EDTA with 6 donor atoms is hexadentate.

#### IUPAC Nomenclature

# Rules for Naming Coordination Compounds

- The cation is named first then the anion.
- In naming coordination sphere, ligands are named first in alphabetical order followed by metal atom and then oxidation state of metal by a roman numeral in parentheses.
- Name of anionic ligands end in -o. e.g, Cl<sup>-</sup>:
   Chlorido, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>: Oxalato etc.
- Neutral ligands (with a few exceptions e.g., H<sub>2</sub>O: aqua) retain their names e.g., NH<sub>3</sub>: Ammine etc.
- Name of cationic ligands end in ium. e.g., NO<sub>2</sub><sup>+</sup>:
   Nitronium etc.

- Certain ligands are represented by abbreviations in parentheses instead of their complex structural formulae. e.g., ethylenediamine (en).
- Ambidentate ligands are named by using different names of ligands or by placing the symbol of donor atom.
  - e.g., —SCN (Thiocyanato-S or Thiocyanato), —NCS (Thiocyanato-N or Isothiocyanato), —ONO (Nitrito-O or Nitrito), —NO<sub>2</sub> (Nitrito-N or Nitro)

#### ISOMERISM IN COORDINATION COMPOUNDS

 Two or more substances having the same molecular formula but different structural or spatial arrangement are called isomers and phenomenon is called isomerism.

#### Isomerism

Ionisation isomerism

Structural Isomerism

Compounds, which give different ions in solution in the number of water due to the exchange of molecules attached to ions in sphere and counter ions as ligands. called ionisation isomers. e.g.,

 $[CoBr(NH_3)_5]SO_4$ and  $[Co(NH_3)_5SO_4]Br$ 

#### Hydrate isomerism

Isomers, which differ coordination the metal atom or ion

> e.g.,  $[Cr(H_2O)_6]Cl_3$  and [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>·H<sub>2</sub>O

> > Shown by

#### Linkage isomerism

When ambidentate ligand attached to metal through different atoms than the compounds are said to be linkage isomers. e.g.,  $[Co(NO_2)(NH_3)_5]Cl_2$ and [Co(ONO)(NH<sub>3</sub>)<sub>5</sub>]Cl<sub>2</sub>

#### Coordination isomerism

Stereoisomerism

When both positive and negative ions of a salt are complex ions and two isomers differ in the distribution of ligands in two complex ions.

e.g.,  $[Co(NH_3)_6][Cr(CN)_6]$ and  $[Co(CN)_6][Cr(NH_3)_6]$ 

trans-

optically inactive

#### Stereoisomerism

#### \* Geometrical or cis-trans isomerism

If two identical ligands occupy adjacent positions  $\Rightarrow$  cis

If occupy opposite positions  $\Rightarrow$  *trans* 

#### In Square Planar C.N.: 4 In Octahedral C.N.: 6

Shown by  $MA_2X_2$  $M(AB)X_2$  $MA_2XY$ MABXY

If all three similar groups occupy adjacent position at the corners of octahedral face then fac-isomer

cis

If three similar groups present around meridian of octahedron then mer-isomer

d-form

cis-optically active

\* Geometrical isomerism is not shown by tetrahedral complexes.

 $M(AA)_2X_2$  and  $MA_4X_2$   $MA_3X_3$ 

trans

#### PEER INTO PREVIOUS YEARS

- The type of isomerism shown by the complex  $[CoCl_2(en)_2]$  is
  - (a) geometrical isomerism
  - (b) coordination isomerism
  - (c) ionization isomerism
  - (d) linkage isomerism.

(NEET 2018)

- As per IUPAC norms, the name of the complex [Co(en)2(ONO)Cl]Cl is
  - (a) Chloridobis(ethane-1,2-diamine)nitro-O-cobalt (III) chloride
  - (b) Chlorobis(ethylenediamine)nitro-Ocobalt(III) chloride

(c) Chloridodi(ethylenediamine)nitrocobalt(III) chloride

Optical isomerism

This isomerism arises due to non-

superimposable mirror images.

Common in octahedral complexes with

2 or 3 bidentate ligands.

l-form

- (d) Chloroethylenediaminenitro-O-cobalt (III) chloride. (Karnataka CET 2016)
- The correct statement on the isomerism associated with the following complex ions,
  - (1)  $[Ni(H_2O)_5(NH_3)]^{2+}$  (2)  $[Ni(H_2O)_4(NH_3)_2]^{2+}$ and (3)  $[Ni(H_2O)_3(NH_3)_3]^{2+}$  is
  - (a) (1) and (2) show only geometrical isomerism
  - (b) (1) and (2) show geometrical and optical isomerism
  - (c) (2) and (3) show geometrical and optical isomerism
  - (d) (2) and (3) show only geometrical isomerism. (JEE Main Online 2015)

#### BONDING IN COORDINATION COMPOUNDS

#### Valence Bond Theory (VBT)

- It was developed by Pauling.
  - A suitable number of vacant orbitals must be present in the central metal atom or ion for the formation of coordinate bonds with the ligands.
  - Central metal ion can use appropriate number of s, p or d-orbitals for hybridisation depending upon the total number of ligands.
- The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether outer d-orbitals or inner d-orbitals are used.
- Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
- Paramagnetism 

  No. of unpaired electrons.
- Magnetic moment =  $\sqrt{n(n+2)}$  B.M. where n = number of unpaired electrons.

Coordination Number	Type of Hybridisation	Geometry	Examples			
2	sp	Linear	[Ag(NH <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> , [Ag(CN) <sub>2</sub> ] <sup>-</sup>			
3	sp <sup>2</sup>	Trigonal planar	[HgI <sub>3</sub> ]			
4	sp <sup>3</sup>	Tetrahedral	Ni(CO) <sub>4</sub> , [Ni $X_4$ ] <sup>2-</sup> , [ZnCl <sub>4</sub> ] <sup>2-</sup> , [Cu $X_4$ ] <sup>2-</sup> , where $X = Cl^-$ , Br <sup>-</sup> , I <sup>-</sup>			
	dsp <sup>2</sup>	Square planar	$[Ni(CN)_4]^{2-}$ , $[Cu(NH_3)_4]^{2+}$ , $[Ni(NH_3)_4]^{2+}$			
E	dsp <sup>3</sup>	Trigonal bipyramidal	Fe(CO) <sub>5</sub> , [CuCl <sub>5</sub> ] <sup>3-</sup>			
3	sp <sup>3</sup> d	Square pyramidal	$[SbF_5]^{2-}$			
6	$d^2sp^3$	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$ , $[Fe(CN)_6]^{3-}$			
	$sp^3d^2$	Octahedral (Outer orbital)	$[FeF_6]^{3-}$ , $[Fe(H_2O)_6]^{2+}$ , $[Ni(NH_3)_6]^{2+}$			

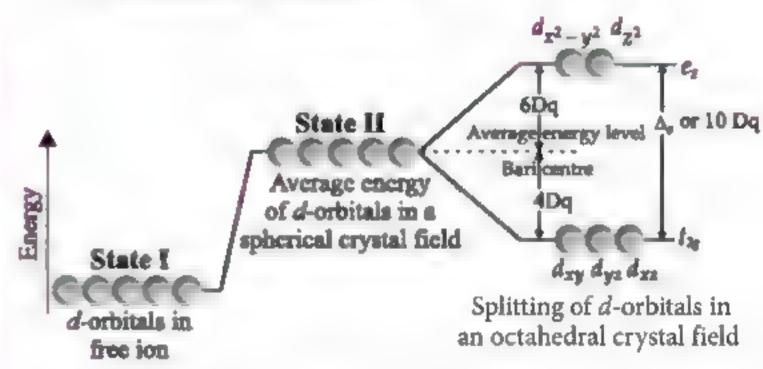
#### Differences between Inner Orbital Complexes and Outer Orbital Complexes

	• •		
Inner Orbital Complexes	Outer Orbital Complexes		
Involves inner $d$ -orbitals i.e., $(n-1)d$ -orbitals.	Involves outer d-orbitals i.e., nd-orbitals		
Low spin complexes	High spin complexes		
Have less or no unpaired electrons, e.g., $[Co(NH_3)_6]^{3+}$ , $[Co(CN)_6]^{4-}$	Have large number of unpaired electrons. <i>e.g.</i> , [MnF <sub>6</sub> ] <sup>3-</sup> , [CoF <sub>6</sub> ] <sup>3-</sup>		

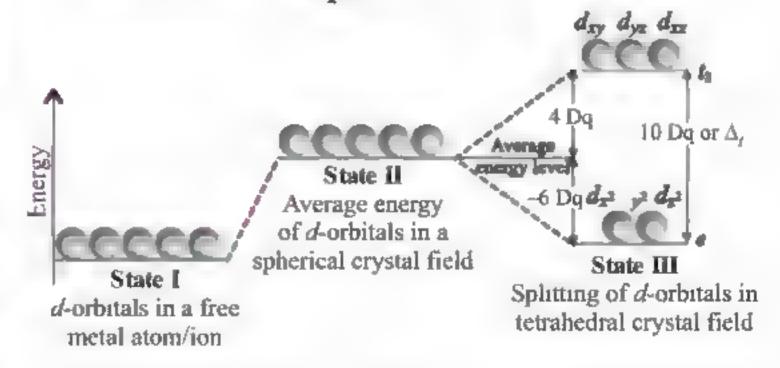
#### **Crystal Field Theory (CFT)**

It assumes the ligands to be point charges and there is electrostatic force of attraction between ligands and metal atom or ion. When ligands approach the central metal ion, then the five degenerate orbitals do not possess equal energy any more and results in splitting, which depends upon nature of ligand field strength. Greater the ease with which the ligand can approach the metal ion, the greater will be the crystal field splitting caused by it.

#### Octahedral Complexes:



#### Tetrahedral Complexes:



- If  $\Delta_o < P$  (where 'P' is energy required for forced pairing of electrons) then the electrons will remain unpaired and a high spin complex is formed.

- If  $\Delta_o > P$ , then pairing of electrons takes place and a low spin complex is formed.
- Difference in energy between e and  $t_2$  level is less in tetrahedral complexes,  $\Delta_t = \frac{4}{9}\Delta_o$

#### Spectrochemical Series

- Ligands are arranged in the order of increasing field strength called spectrochemical series.
- $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < S^{2-} <$  $H_2O < NCS^- < EDTA^{4-} < NH_3 < en < NO_2^- < CN^- < CO^-$ Strong field Weak field Increasing order of CFSE ligand ligand

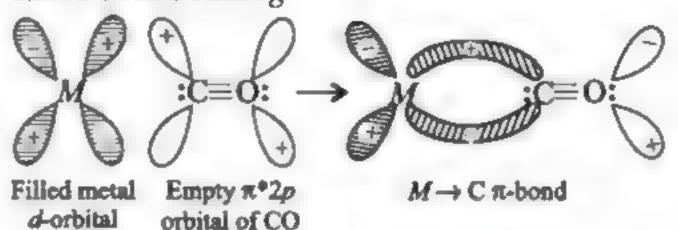
#### BONDING IN METAL CARBONYLS

Metal-carbon bond in metal carbonyls possesses both  $\sigma$ - and  $\pi$ -character. Its formation involves following steps:

There is an overlap of filled  $\pi_{2p}$  orbital of CO with suitable empty metal orbital resulting in the formation of σ- bond.

$$C \equiv O: \longrightarrow OM \bigcirc C \equiv O:$$
Vacant | Containing |  $M \leftarrow C \sigma$ -bond | lone pair

 $\pi$ -overlap involving filled metal d-orbital and empty antibonding  $\pi^*2p$  orbital of same CO. This results in formation of  $M \to C \pi$ -bond. This is also called back bonding.



#### STABILITY OF COORDINATION COMPOUNDS

Charge on the central metal ion (oxidation state): Greater the charge on central metal ion, more is the stability.

Basic nature of ligand: More the basic strength of ligand, more is the stability of complex.

Presence chelate rings: Formation of chelate ring the increases stability of complex.

Size the metal ion Smaller size of metal ion, more is the stability.

Electronegativity and polarising power of the central metal ion: More is the electronegativity and polarising power of the metal ion, more stable is the complex.

#### **Applications of Coordination Compounds**

- Coordination compounds are of great importance in biological system. e.g., chlorophyll, haemoglobin, vitamin B<sub>12</sub>, etc. are coordinate compounds of Mg, Fe and Co respectively.
- Coordination compounds are used for qualitative and quantitative analysis, extraction of metals, electroplating, photography and as dyes.
- cis-Platin is used in cancer treatment, EDTA is often used for treatment of lead poisoning.
- Coordination compounds are used as catalyst.

#### PEEP INTO PREVIOUS YEARS

- 10. What is the correct electronic configuration of the central atom in  $K_4[Fe(CN)_6]$  based on crystal field theory?
  - (a)  $e^4t_2^2$

- (b)  $t_{2g}^4 e_g^2$  (c)  $t_{2g}^6 e_g^0$  (d)  $e^3 t_2^3$ (NEET 2019)

- 11. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28)
  - (a) total number of valence shell electrons at metal centre in Fe(CO)<sub>5</sub> or Ni(CO)<sub>4</sub> is 16
  - (b) these are predominantly low spin in nature
  - (c) metal-carbon bond strengthens when the oxidation state of the metal is lowered
  - (d) the carbonyl C O bond weakens when the oxidation state of the metal is increased.

(JEE Advanced 2018)

12. The correct order of spin-only magnetic moments among the following is

(Atomic number: Mn = 25, Co = 27, Ni = 28, Zn = 30)

- (a)  $[ZnCl_4]^{2-} > [NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$
- (b)  $[CoCl_4]^{2-} > [MnCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$
- (c)  $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [NiCl_4]^{2-} > [ZnCl_4]^{2-}$ (d)  $[NiCl_4]^{2-} > [CoCl_4]^{2-} > [MnCl_4]^{2-} > [ZnCl_4]^{2-}$

#### Points For Extra Scoring

- Different complexes exhibit different colours when either the metal ion is different or the metal ion is same but the ligands attached to it are different.
- **Effective Atomic Number Rule (EAN Rule):** EAN = Atomic No. of metal - No. of electrons lost in ion formation + No. of electrons gained from ligands
- Irving-Williams order: Irrespective of the nature of the ligand, the stability of the divalent metal ions of the first transition series is in the following order: Mn (II) < Fe (II) < Co (II) < Ni (II) < Cu (II) < Zn (II)
- Calculation of CFSE : CFSE =  $(-0.4x + 0.6y) \Delta_o$ where,  $x = \text{No. of electrons in } t_{2g}$  $y = \text{No. of electrons in } e_g$

#### In octahedral complexes

Strong field ligand  $\rightarrow$  High  $\Delta_0$  value  $\rightarrow$  Low spin complexes

Weak field ligand  $\rightarrow$  Low  $\Delta_0$  value  $\rightarrow$  High spin complexes

- Colour of the coordination compound is due to d-d transition.
- Large  $\Delta_o$  = higher energy light absorbed (shorter wavelengths)

Smaller  $\Delta_o$  = lower energy light absorbed (longer wavelengths)

- Chelating ligands give much larger values of stability constant.
- The numerical value of stability constant is a measure of stability of the complex in solution, greater the magnitude of the stability constant more stable is the complex.

#### **Answer Key For Peep Into Previous Years**

- (a) (b,d) 2.
- (a) 10. (c) (b,c)11.



- 1. Anhydrous ferric chloride is prepared by
  - (a) heating hydrated ferric chloride at a high temperature in a stream of air
  - (b) heating metallic iron in a stream of dry chlorine gas
  - (c) reaction of ferric oxide with hydrochloric acid
  - (d) reaction of metallic iron with dilute hydrochloric acid.
- 2. If the lanthanoid ion  $(M^{3+})$  with xf-electrons has a pink colour, then the lanthanoid ion with (14 - x)f-electrons will have the colour as
  - (a) blue
- (b) red
- (c) green (d) pink.
- 3. Mixture X containing 0.02 mol of [Co(NH<sub>3</sub>)<sub>5</sub>SO<sub>4</sub>]Br and 0.02 mol of [Co(NH<sub>3</sub>)<sub>5</sub>Br]SO<sub>4</sub> was prepared in 2 litre of solution.
  - 1 litre of mixture  $X + \text{excess AgNO}_3 \longrightarrow Y$
  - 1 litre of mixture  $X + \text{excess BaCl}_2 \longrightarrow Z$

- Number of moles of Y and Z are respectively
- (a) 0.01, 0.01
- (b) 0.02, 0.01
- (c) 0.01, 0.02
- (d) 0.02, 0.02
- Which of the following complexes exists as pair of enantiomers?
  - (a) trans-[Co(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>
  - (b)  $[Co(NH_3)_4Cl_2]^+$
  - (c)  $[Co{P(C_2H_5)_3}_2ClBr]$
  - (d)  $[Cr(en)_3]^{3+}$
- CrO<sub>3</sub> dissolves in aqueous NaOH to give
  - (a)  $CrO_4^{2-}$
- (b)  $Cr(OH)_3$
- (c)  $Cr_2O_7^{2-}$
- (d)  $Cr(OH)_2$
- When copper sulphate solution is added to potassium ferrocyanide, the formula of product obtained is
  - (a)  $Cu_2[Fe(CN)_6]$
- (b) Cu(CN)<sub>3</sub>
- (c) CuFe(CN)<sub>6</sub>
- (d)  $Cu(CN)_2$

- The coordination number of a central metal atom/ ion in a complex is determined by
  - (a) the number of ligands around a metal atom/ion bonded by sigma bonds
  - (b) the number of only anionic ligands bonded to the metal atom/ion
  - (c) the number of ligands around a metal atom/ion bonded by both sigma and pi-bonds
  - (d) the number of ligands around a metal atom/ion bonded by pi-bonds.
- Which of the following pair contains metals in their highest oxidation states?
  - (a)  $MnO_2$ ,  $TiO_3$
  - (b)  $[MnO_4]^-$ ,  $CrO_2Cl_2$
  - (c)  $[Fe(CN)_6]^{4-}$ ,  $[Co(CN)_6]^{3-}$
  - (d)  $[NiCl_4]^{2-}$ ,  $[CoCl_4]^{-}$
- 9. Which one of the following cyano complex would exhibit the lowest value of paramagnetic behaviour?

  - (a)  $[Cr(CN)_6]^{3-}$  (b)  $[Co(CN)_6]^{3-}$

  - (c)  $[Fe(CN)_6]^{3-}$  (d)  $[Mn(CN)_6]^{3-}$
- 10. Low spin complex of  $d^6$ -cation in an octahedral field will have the following energy  $(\Delta_o = \text{crystal field splitting energy in an octahedral})$ field, P = electron pairing energy)

  - (a)  $\frac{-12}{5}\Delta_o + P$  (b)  $\frac{-12}{5}\Delta_o + 3P$
  - (c)  $\frac{-2}{5}\Delta_o + 2P$  (d)  $\frac{-2}{5}\Delta_o + P$
- 11. Assertion: F ion is a weak ligand and forms outer orbital complex.

**Reason**:  $F^-$  ion cannot force the electrons of  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals of the inner shell to occupy  $d_{xy}$ ,  $d_{yz}$ and  $d_{zx}$  orbitals of the same shell.

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 12. The colourless species is
  - (a) VCl<sub>3</sub>
- (b) VOSO<sub>4</sub>
- (c)  $Na_3VO_4$  (d)  $[V(H_2O)_6SO_4]H_2O$
- 13. Copper sulphate is dissolved in water containing for making Bordeaux mixture.
  - (a) NaOH
- (b) KCN
- (c) Ca(OH)<sub>2</sub>
- (d) all of these

- 14. In the standardization of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> by iodometry, the equivalent weight of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is
  - (a) (molecular weight)/2
  - (b) (molecular weight)/6
  - (c) (molecular weight)/3
  - (d) same as molecular weight.
- 15. Ammonia forms the complex ion  $[Cu(NH_3)_4]^{2+}$  with copper ions in alkaline solution but not in acidic solution. What is the reason for it?
  - (a) In acidic solutions hydration protects copper ions.
  - (b) In acidic solutions protons coordinate with ammonia molecules forming NH4<sup>+</sup> ions and NH<sub>3</sub> molecules are not available.
  - (c) In alkaline solutions insoluble Cu(OH)2 is precipitated which is soluble in excess of any alkali.
  - (d) Copper hydroxide is an amphoteric substance.
- 16. Which of the following does not have a metal-carbon bond?
  - (a)  $K[Pt(C_2H_4)Cl_3]$  (b)  $Ni(CO)_4$

  - (c)  $Al(OC_2H_5)_3$  (d)  $C_2H_5MgBr$
- 17. The EAN of metal atoms in  $K_3[Cr(C_2O_4)_3]$  and Co<sub>2</sub>(CO)<sub>8</sub> respectively are

  - (a) 34, 35 (b) 34, 36 (c) 33, 36 (d) 36, 35

- 18. A white crystalline salt A reacts with dilute HCl to liberate a suffocating gas B and also forms a yellow precipitate. The gas B turns potassium dichromate acidified with dilute H<sub>2</sub>SO<sub>4</sub> to a green coloured solution C. A, B and C are respectively
  - (a)  $Na_2SO_3$ ,  $SO_2$ ,  $Cr_2(SO_4)_3$
  - (b)  $Na_2S_2O_3$ ,  $SO_2$ ,  $Cr_2(SO_4)_3$
  - (c)  $Na_2S$ ,  $SO_2$ ,  $Cr_2(SO_4)_3$
  - (d) Na<sub>2</sub>SO<sub>4</sub>, SO<sub>2</sub>, Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>
- 19. The correct IUPAC name of the compound  $[Cr(NH_3)_5(NCS)]$   $[ZnCl_4]$ , is
  - (a) pentaammineisothiocyanatochromium(III)
    - tetrachloridozincate(II)
  - (b) pentaammineisothiocyanatozinc(II)

chloridochromate(III)

Monthly	Test Drive	CLASS XI	DANSW	ER KEY
1. (c)	2. (c)	<b>3.</b> (b)	<b>4.</b> (a)	5. (a)
6. (d)	7. (c)	8. (d)	9. (a)	<b>10.</b> (b)
11. (d)	12. (c)	13. (a)	14. (c)	15. (a)
16. (b)	17. (a)	18. (d)	19. (a)	<b>20.</b> (b,c,d)
<b>21.</b> (a,b)	<b>22.</b> (b,d)	23. (a,b,c)	<b>24.</b> (4)	<b>25.</b> (2)
<b>26.</b> (5)	27. (a)	28. (d)	<b>29.</b> (d)	<b>30.</b> (a)

- (c) pentaammineisothiocyanatochromate(II) tetrachloridozincate(II)
- (d) isothiocyanatopentaamminechromium(II) chloridozinc(IV).
- 20. When AgCl is treated with KCN
  - (a) Ag is precipitated
  - (b) a complex ion is formed
  - (c) double decomposition takes place
  - (d) no reaction takes place.

#### SOLUTIONS

1. (b): Anhydrons FeCl<sub>3</sub> cannot be prepared by heating hydrated salt, because it decomposes to Fe<sub>2</sub>O<sub>3</sub> on heating.

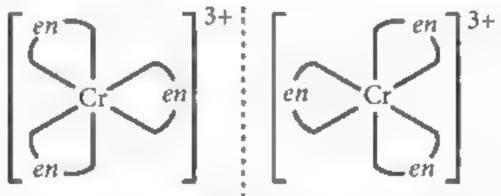
Reaction of ferric oxide with hydrochloric acid gives hydrated FeCl<sub>3</sub>.

Reaction of metallic iron with dilute HCl produces FeCl<sub>2</sub> and H<sub>2</sub>.

- 2. (d): In case of lanthanoids  $M^{3+}$  ion, the element with xf electrons has a similar colour to that of (14-x)f electrons.
- 3. (a):  $[Co(SO_4)(NH_3)_5]Br + Ag^+(excess) \rightarrow 0.01 \text{ mol/L}$  from  $AgNO_3$   $[Co(SO_4)(NH_3)_5]^+ + AgBr_{(s)}$  0.01 mol

 $[CoBr(NH_3)_5]SO_4 + Ba^{2+}_{(aq)} \rightarrow [CoBr(NH_3)_5]^{2+} + BaSO_{4(s)}$ 0.01 mol/L from BaCl<sub>2</sub> 0.01 mol

4. (d): Optical isomers rarely occur in square planar complexes on account of presence of axis of symmetry. Optical isomerism is very common in octahedral complexes of the formula,  $[Ma_2b_2c_2]^{n\pm}$ ,  $[Mabcdef]^{n\pm}$ ,  $[M(AA)_3]^{n\pm}$ ,  $[M(AA)_2a_2]^{n\pm}$ ,  $[M(AA)_2ab]^{n\pm}$  and  $[M(AB)_3]^{n\pm}$ . Thus, among the given compounds, only  $[Cr(en)_3]^{3+}$  exhibits optical isomerism and exists as a pair of enantiomers.

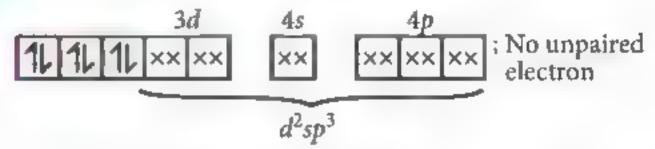


- 5. (a):  $CrO_3 + 2NaOH \longrightarrow Na_2CrO_4 + H_2O$
- 6. (a):  $2\text{CuSO}_4 + \text{K}_4[\text{Fe}(\text{CN})_6]$   $\longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6] + 2\text{K}_2\text{SO}_4$ Reddish brown ppt.
- 7. (a): The coordination number of the central atom or ion is determined by the number of sigma bonds between the ligands and the central atom/ion.
- 8. (b): The oxidation states of Mn in  $MnO_4^-$  is +7 and Cr in  $CrO_2Cl_2$  is +6.

So, the pair [MnO<sub>4</sub>], CrO<sub>2</sub>Cl<sub>2</sub> has the metals in their highest oxidation states.

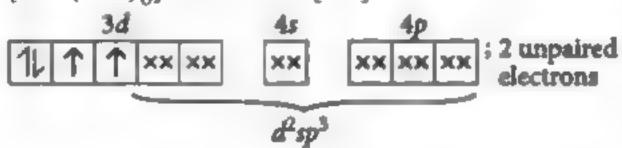
9. (b):  $CN^-$  is a strong field ligand, thus, causes pairing of electrons in 3d-orbitals.

 $[Co(CN)_6]^{3-}$ :  $Co^{3+}$ : [Ar]3 $d^6$ 



 $[Fe(CN)_6]^{3-}$ :  $Fe^{3+}$ :  $[Ar]3d^5$ 

 $[Mn(CN)_6]^{3-}:Mn^{3+}:[Ar]3d^4$ 



Greater the number of unpaired electrons, higher is the paramagnetism.

10. (b): C.F.S.E. =  $(-0.4x + 0.6y)\Delta_o + zP$ where x = number of electrons occupying  $t_{2g}$  orbital y = number of electrons occupying  $e_g$  orbital z = number of pairs of electrons

For low spin  $d^{\delta}$  complex electronic configuration

$$= t_{2g}^{6} e_{g}^{0} \text{ or } t_{2g}^{2,2,2} e_{g}^{0}$$

$$\therefore x = 6, y = 0, z = 3$$
C.F.S.E. =  $(-0.4 \times 6 + 0 \times 0.6)\Delta_{o} + 3P = \frac{-12}{5}\Delta_{o} + 3P$ 
11. (a)

- 12. (c):  $Na_3VO_4$  contains vanadium in +5 oxidation state which has empty d-orbitals and is thus colourless.
- 13. (c): Bordeaux mixture consists of copper sulphate (CuSO<sub>4</sub>) and slaked lime [Ca(OH)<sub>2</sub>].
- 14. (b): Potassium dichromate is used to standardise sodium thisulphate solution. In acidic solution, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>

# Quotable Quote

I don't care that they stole my idea ...
I care that they don't have any of their own.

**NIKOLA TESTA** 

oxidises KI to iodine, the iodine thus generated can then be titrated with thiosulphate solution using starch indicator.

$$Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

 $\therefore \quad \text{Equivalent weight of } K_2Cr_2O_7 = \frac{\text{Molecular weight}}{6}$ 

15. (b):: NH<sub>3</sub> molecule acts as a base due to the presence of a lone pair of electrons on it. In acidic medium, it accepts a proton to form NH<sub>4</sub><sup>+</sup> ion, hence it does not have a lone pair of electrons on N-atom. Therefore, it cannot act as a ligand.

$$:NH_3 + H^+ \longrightarrow NH_4^+$$

16. (c): In Al(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, aluminium atom is bonded to  $C_2H_5$  group through oxygen.

17. (c): 
$$K_3[Cr(C_2O_4)_3]$$
; EAN =  $(24-3)+6\times 2=33$   
 $Co_2(CO)_8$ ; EAN =  $27+1$  (1 electron shared from

another Co atom) + 8 (8 electrons from 4 CO molecules) = 36

18. (b): Dilute HCl decomposes  $Na_2S_2O_3(A)$  with evolution of a gas which possesses a suffocating smell of burning sulphur *i.e.*,  $SO_2(B)$  and yellow ppt. of sulphur is obtained.

$$Na_2S_2O_3 + 2HCl \longrightarrow 2NaCl + SO_2 \uparrow + S \downarrow + H_2O$$
(A) (Yellow ppt.)

When acidified potassium dichromate paper is exposed to the gas, it attains a green colour due to the formation of chromium sulphate.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

(C)

Green

19. (a)

20. (b): 
$$AgCl + 2KCN \longrightarrow KAg[(CN)_2] + KCl$$





## Science Behind Indian Customs



#### Do not take bath immediately after eating

If a person is immediately taking bath after a meal, the digestion process gets slowed down as cold water activates certain chemicals in the body that rushes the blood to the skin to keep it warm and the digestion process takes a backseat. Bath will increase blood flow to the hands, feet and body because of which the amount of blood around the stomach will continue to decrease. This will weaken the digestive system in our stomach. So, it was always advised by our ancestors to take food after having a bath.

#### The act of putting water around the plate

We know water acts as a repe lent to many tiny creatures that roam on the floor seen and unseen, hence the circle of water stops them to approach the plate when kept on the floor. Also they are attracted towards the part of food kept outside the plate for birds as per the Indian customs, thus making it safe to consume our food. This practice is redundant while eating on dining table which is presumable cleaner than the floor. Those who still practice it on table are just following tradition without knowing the meaning behind it.





# Why do elders rotate crystal salt, lemon around head to prevent from an evil eye?

An evil eye (negative energy) creates unwanted magnetic field around us which affect our health. Salt can be considered as the first antibiotic. Not only that, the salty and acidic substances have the properties to keep away from these unwanted magnetic field. When the sat and lemon revolved around a person, it forms an aura layer of antibiotics and would kill all the bacteria. Not only has this, revolving around the person balance the magnetic field too. This would make the person feel better.

#### Scientific reason behind hanging leaves on doors

t is common practice in india to decorate the main door of the house, temples with a garland of leaves. It may just be a ritual but there is a more scientific meaning behind the hanging of these leaves. The garland is made preferably of fresh and green mango leaves for their aesthetically pleasing appearance but neem leaves are also included most of the time. As we know, green leaves absorb carbon dioxide and release oxygen. This helps in keeping the surrounding atmosphere clean and hygienic. The green colour is also soothing and refreshing to the mind. Having a garland of leaves at the doorstep can be a small way of relaxing and unwinding from stress.





Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2019-20.

#### Series 5

Haloalkanes and Haloarenes I Alcohols, Phenois and Ethers Time Allowed: 3 hours Maximum Marks: 70

#### **GENERAL INSTRUCTIONS**

- All questions are compulsory.
- (ii) Section A: Q. no. 1 to 20 are very short answer-objective questions and carry 1 mark each.
- (iii) Section B: Q. no. 21 to 27 are short answer questions and carry 2 marks each.
- (iv) Section C: Q. no. 28 to 34 are long answer-I questions and carry 3 marks each.
- (v) Section D: Q. no. 35 to 37 are long answer-II questions and carry 5 marks each.
- (vi) There is no overall choice in the question paper. However, internal choices are given in the sections.
- (vii) Use log tables if necessary, use of calculator is not allowed.

#### SECTION-A

1. In  $S_N^2$  substitution reaction of the type,  $R - Br + Cl^{-} \xrightarrow{DMF} R - Cl + Br^{-}$ which one of the following has the highest relative rate?

(a) 
$$CH_3 - C - CH_2Br$$
 (b)  $CH_3CH_2Br$   $CH_3$ 

- Conversion of chlorobenzene to phenol involves
  - (a) electrophilic substitution
  - (b) nucleophilic substitution
  - (c) free radical substitution
  - (d) electrophilic addition.
- 3. The correct increasing order of reactivity for the given molecules towards electrophilic aromatic substitution is

$$\begin{array}{c|ccccc}
OH & OH & OH & OH \\
\hline
OO & OMe & OH & OH \\
\hline
OOMe & OOMe & OH \\
\hline
OOMe & OOMe & OOMe \\
\hline
OOMe & OOMe \\
\hline
OOMe & OOMe & OOMe \\
\hline
OOMe &$$

- (a) I < IV < II < III (b) I < IV < III < II
- (c) I < III < II < IV
  - (d) I < III < IV < II
- The products obtained when anisole is heated in a sealed tube with HI are

- Which of the following compounds on oxidation gives ethyl methyl ketone?
  - (a) 2-propanol
- (b) 1-butanol
- (c) 2-butanol
- (d) t-butyl alcohol

- 6. An ether is more volatile than an alcohol having the same molecular formula. This is due to
  - (a) dipolar character of ethers
  - (b) alcohols having resonance structures
  - (c) intermolecular hydrogen bonding in ethers
  - (d) intermolecular hydrogen bonding in alcohols.
- 7. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is
  - (a) 2
- (b) 3
- (c) 4
- (d) 1
- Chloroform on reaction with conc. HNO<sub>3</sub> gives
  - (a) chloropicrin
- (b) nitromethane
- (c) picric acid
- (d) acetylene.
- 9.  $R CH_2 Br + AgCN \xrightarrow{alcohol} Z$  (Major product) The product Z may be

  - (a)  $R CH_2 CN$  (b)  $R CH_2 NC$
  - (c)  $R-CH_2-CH_2-CN$  (d)  $R-CH_2-CH_2-NC$
- 10. The IUPAC name of the compound,
  - HO (a) 3,3-dimethyl-1-hydroxy cyclohexane
  - (b) 1,1-dimethyl-3-hydroxy cyclohexane
  - (c) 3,3-dimethyl-1-cyclohexanol
  - (d) 1,1-dimethyl-3-cyclohexanol.
- 11. Arrange the following halides in order of increasing S<sub>N</sub>2 reactivity.

CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>CH<sub>2</sub>Cl, (CH<sub>3</sub>)<sub>2</sub>CHCl

- 12. Identify the major product of the following reaction Me  $\longrightarrow$  I + Cu  $\stackrel{\triangle}{\longrightarrow}$
- 13. Explain the following:

Alkyl halides, though polar, are immiscible with (AI 2017C, Foreign 2015, Delhi 2013C, water. AI 2013C, 2012C, 2010C)

14. Suggest the most probable product of the following reaction:

$$CH_3-CH=CH_2 \xrightarrow{(i) B_2H_6} (ii) H_2O_2/OH$$

- 15. What happens when benzenesulphonic acid is fused with NaOH followed by hydrolysis?
- Write the IUPAC name of the given compound.  $CH_2 = C - CH_2 - OH$

(AI 2015)

17. Predict the product.

- 18. What is the order of dehydration of 1°, 2° and 3° alcohols?
- 19. Why CHF<sub>3</sub> is less acidic than CHCl<sub>3</sub> though fluorine is more electronegative than chlorine?
- 20. What will be the order of boiling points of different alkyl halides containing same alkyl group?

#### SECTION-B

- 21. Haloarenes are less reactive than haloalkanes. Explain.
- 22. How do you convert:
  - (i) Chlorobenzene to biphenyl
  - (ii) 2-Bromobutane to but-2-ene?
- 23. How are the following conversions carried out:
  - (i) Benzyl chloride to benzyl alcohol
  - (ii) Propene to 1-iodopropane?
- 24. How is methanol manufactured? Give one use of methanol.
- 25. Give reasons:
  - (i) Racemic mixture is optically inactive.
  - (ii) The presence of nitro group (-NO<sub>2</sub>) at o/p positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.

(Delhi 2015)

#### OR

Write the structures and names of the compounds formed when compound 'A' with molecular formula,  $C_7H_8$  is treated with  $Cl_2$  in the presence of FeCl<sub>3</sub>.

- **26.** Account for the following:
  - (i) Phenols do not give protonation reactions readily.
  - (ii) Alcohols act as Bronsted acid and Bronsted base both.

#### OR

Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols. Give reason.

- 27. Write a chemical test to distinguish between:
  - (i) Chlorobenzene and benzyl chloride
  - (ii) Chloroform and carbon tetrachloride

#### SECTION-C

28. Compound 'A' with molecular formula C<sub>4</sub>H<sub>9</sub>Br is treated with aqueous KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When an optically active isomer 'B' of this compound was treated with aqueous KOH solution, the rate of reaction was found to be

dependent on concentration of compound 'B' and KOH both.

- (i) Write down the structural formula of both compounds 'A' and 'B'.
- (ii) Out of these two compounds, which one will be converted to the product with inverted configuration?
- 29. (i) What happens when phenol is treated with bromine water?
  - (ii) Write the equation involved in the following reactions:
    - (a) Kolbe's reaction
    - (b) Reimer-Tiemann reaction

#### OR

What happens when

- (i) ethyl alcohol reacts with red P and Br<sub>2</sub>?
- (ii) anisole is treated with Br<sub>2</sub> in CH<sub>3</sub>COOH?
- (iii) 3°alcohol is treated with KMnO<sub>4</sub> at high temperature?
- 30. (i) Is it desirable to synthesise alcohols in a copper vessel?
  - (ii) Draw the structures of all the isomeric alcohols of molecular formula C<sub>5</sub>H<sub>12</sub>O, give their IUPAC names. Classify them as 1°, 2° and 3° alcohols.
- 31. A sweet smelling organic compound 'A' is slowly oxidised by air in the presence of light to a highly poisonous gas. On warming with silver powder it forms a gaseous substance 'B' which is also produced by the action of calcium carbide on water. Identify 'A' and 'B' and write the equations of the reactions involved.
- 32. (a) Identify the chiral molecule in the following pair:

- (b) Write the structure of the product when chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether.
- (c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1-methylcyclohexane with alcoholic KOH. (2018)

#### OR

(a) A chloro derivative (A) on treatment with zinc-copper couple gives a hydrocarbon with five carbon atoms. When (A) is dissolved in ether and treated with sodium then 2, 2, 5, 5

- -tetramethylhexane is obtained. What is the original compound (A)?
- (b) Draw the structure of major monohalogen product in the following reaction:

- 33. (a) Give chemical tests to distinguish between the following pairs of compounds:
  - (i) Pentan-2-ol and pentan-3-ol
  - (ii) Ethanol and phenol
  - (b) o-Nitrophenol is more acidic than o-methoxyphenol. Explain why.
- 34. How would you convert the following:
  - (i) Phenol to benzoquinone
  - (ii) Propanone to 2-methylpropan-2-ol
  - (iii) Propene to propan-2-ol

#### SECTION D

- 35. (a) Phenol is acidic while hexanol is neutral towards a solution of NaOH. Why?
  - (b) m-Aminophenol is stronger acid than o-aminophenol. Explain.
  - (c) Name the different reagents needed to perform the following reactions:
    - (i) Phenol to benzene
    - (ii) Friedel-Crafts alkylation of anisole
    - (iii) Dehydrogenation of ethanol to ethanal

#### OR

- (i) Write the structure of the products when butan-2-ol reacts with the following:
  - (a) CrO<sub>3</sub>
- (b) SOCl<sub>2</sub>
- (ii) How is 1-propoxypropane synthesised from propan-1-ol? Give mechanism.
- 36. (a) The following reaction proceeds by an  $S_N^2$  pathway:

$$C_6H_5CH_2Br + NaN_3 \longrightarrow C_6H_5CH_2N_3 + NaBr$$

- (i) Write an equation for the expected rate constant.
- (ii) Draw a potential energy diagram for the reaction.
- (iii) How would the rate of the reaction change if concentration of sodium azide is doubled?
- (b) Write the mechanism of the following reaction:

$$n$$
-BuBr + KCN  $\xrightarrow{\text{EtOH, H}_2\text{O}} n$ -BuCN

#### OR

Complete the following reactions:

- (a)  $CH_3CH_2COOAg \xrightarrow{Br_2} ? \xrightarrow{alc KOH} ?$
- (b)  $CH_3CH_2CH_2Cl \xrightarrow{CH_3C \equiv CNa}$ ?

(c) 
$$CH_2$$
— $CH = CH_2 + HBr \xrightarrow{Peroxide}$ ?

(d) 
$$CH_3CHI \xrightarrow{Na} ?$$
  $CH_3$   $CH_3$ 

(e) 
$$CH_3CH = CH_2 \xrightarrow{HBr} ? \xrightarrow{aq. KOH} ?$$

- 37. (a) Phenols are stronger acids than alcohols, why?
  - (b) Draw resonance structures of phenol and phenoxide ion.
  - (c) What is aspirin? How is aspirin prepared?

#### OR

- (a) How do you convert the following:
  - (i) Phenol to anisole
  - (ii) Ethanol to propan-2-ol
- (b) Write mechanism of the following reaction:  $C_2H_5OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$
- (c) Why phenol undergoes electrophilic substitution more easily than benzene? (Delhi 2019)

#### SOLUTIONS

- 1. (b) 2. (b
- 3. (b): Greater is the electron density on aromatic ring, greater is the reactivity towards electrophilic aromatic substitution.

5. (c) : 
$$CH_3CH(OH)CH_2CH_3 \xrightarrow{[O]} CH_3CCH_2CH_3$$
2-Butanol Ethyl methyl ketone

6. (d): The reason for the lesser volatility of alcohols than ethers is the intermolecular association of a large number of alcohol molecules due to hydrogen bonding as —OH group is highly polarised.

No such hydrogen bonding is present in ethers.

- 7. (a)
- 8. (a) : CHCl<sub>3</sub> + HNO<sub>3</sub> ----> CCl<sub>3</sub>NO<sub>2</sub> + H<sub>2</sub>O
  Chloropicrin
- 9. (b) 10. (c)
- 11. Order of increasing S<sub>N</sub>2 reactivity:
  CH<sub>3</sub>Br > CH<sub>3</sub>Cl > CH<sub>3</sub>CH<sub>2</sub>Cl > (CH<sub>3</sub>)<sub>2</sub>CHCl

12. 
$$2Me - O - I \xrightarrow{Cu} Me - O - Me$$

13. Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular

H-bond among water molecules is much higher than energy released by water halide interaction.

14. 
$$CH_3$$
— $CH=CH_2$   $\xrightarrow{(1) B_2 H_6}$   $CH_3$ — $CH_2$ — $CH_2$ OH

Propene Propan-1-ol

15. When benzene sulphonic acid is fused with NaOH, sodium phenoxide is formed which on hydrolysis yields phenol.

16. 2-Methylprop-2-en-1-ol

17. 
$$CH_3$$
  $C-Br + Na^{\dagger}O - CH_3$ 
 $CH_3$ 
 $CH_3$ 

- 18.  $3^{\circ} > 2^{\circ} > 1^{\circ}$  (order of dehydration of alcohol)
- 19.  $\overline{CCl_3}$  obtained by the removal of proton from  $CHCl_3$  is stabilized by resonance due to the presence of d-orbitals in chlorine while  $\overline{CF_3}$  is not stabilized by resonance due to absence of d-orbitals in fluorine.
- **20.** Order of increasing boiling points of alkyl halides : R I > R Br > R Cl > R F
- 21. In haloarenes, the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring.
- C Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore they are less reactive towards nucleophilic substitution reaction.

Benzyl chloride

Benzyl alcohol

$$\begin{array}{c} \xrightarrow{\text{Nal}} & \text{CH}_3 - \text{CH}_2 - \text{CH}_2 \text{I} \\ & \text{1-Iodopropane} \end{array}$$

24. Methanol is manufactured by catalytic hydrogenation of carbon monoxide at high pressure and temperature.

$$CO + 2H_2 \xrightarrow{ZnO-Cr.O_3} CH_3OH$$

Methanol is chiefly used for the preparation of formaldehyde.

- 25. (i) Racemic mixture contains equal amount of d- and l-forms, hence rotation due to one enantiomer is cancelled by another.
- (ii) The presence of nitro group at o-and p-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

- 26. (i) Due to electron withdrawing effect of phenyl group, the electron density on the oxygen atom of -OH group in phenol is less. Hence phenols do not undergo protonation.
- (ii) Due to presence of lone pair of electrons on oxygen atom, alcohols accept a proton which makes them Bronsted base and due to acidic hydogen they donate the proton to strong base which makes them Bronsted acid.

#### OR

The order of reactivity of alcohols with sodium metal is of the order: Primary > Secondary > Tertiary.

Electron releasing inductive effect of alkyl group in alcohols increases the electron density around O-H bond which makes the O-H bond stronger and makes the alcohol a weaker acid. Therefore more the number of alkyl groups, stronger is the O-H bond and weaker acid is the alcohol.

- 27. (i) Benzyl chloride gives white precipitate with AgNO, solution while chlorobenzene does not.
- (ii) CHCl<sub>3</sub> with aniline in presence of alc. KOH gives foul smelling isocyanides whereas CCl<sub>4</sub> does not.

28. (i) 
$$CH_3$$
 $CH_3$ 
 $CH_3$ 

2 Bromo-2-methylpropane

CH<sub>3</sub>CH<sub>2</sub>CH - CH<sub>3</sub> 
$$\xrightarrow{aq. \text{ KOH}}$$
 CH<sub>3</sub>CH<sub>2</sub>CH - CH<sub>3</sub>

Br

(B)

2-Bromobutane
(Optically active)

- (ii) Compound (B) will be converted to product with inverted configuration as it undergoes  $S_N^2$  nucleophilic substitution. Compound (A) being a tertiary halide, undergoes  $S_N^1$  substitution which is accompanied by racemisation.
- 29. (i) When phenol is treated with bromine water, 2, 4, 6-tribromophenol is formed.

(ii) (a) Kolbe's reaction:

(b) Reimer-Tiemann reaction:

(i) Ethyl alcohol on reaction with red P and Br<sub>2</sub> gives ethyl bromide.

(ii) Anisole on treatment with bromine in acetic acid produces a mixture of p-bromoanisole and o-bromoanisole.

(iii) 3° alcohol reacts with KMnO<sub>4</sub> at high temperature to give carboxylic acid having lesser number of carbon atoms.

$$CH_{3} - C - CH_{2} - CH_{3} \xrightarrow{KMnO_{4}}$$

$$CH_{3} - C - CH_{2} - CH_{3} \xrightarrow{CH_{3}}$$

$$CH_{3} - C - CH_{2} - CH_{3} \xrightarrow{CH_{3}}$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

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$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

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$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

$$CH_{3} - C - CH_{3} = O + CH_{3}COOH$$

30. (i) It is not desirable to synthesise alcohols in copper vessel as it can undergo oxidation or dehydration.

$$CH_3CH_2OH \xrightarrow{Cu, \Delta} CH_3CHO$$
  
 $(CH_3)_2CHOH \xrightarrow{Cu, \Delta} (CH_3)_2C = O$   
 $(CH_3)_3COH \xrightarrow{Cu, \Delta} (CH_3)_2C = CH_2$ 

 $(2^{\circ})$ 

2-Methylbutan-2-ol

31. The sweet smelling organic compound 'A' is chloroform (CHCl<sub>3</sub>). Its chemical reactions are as follows:

Phosgene is a highly poisonous gas. The action of chloroform with silver powder gives acetylene (B).

Calcium carbide when reacted with water also gives acetylene.

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + CH \equiv CH$$
Calcium carbide

Acetylene

Chlorobenzene

(c) 
$$\left\langle \begin{array}{c} Br \\ CH_3 \end{array} \right\rangle$$

1-Bromo-1-methylcyclohexane

$$CH_3 + CH_2$$
 $C(major)$   $(minor)$ 

OR

(a) 
$$CH_3$$
  $CH_3$   $CH_3$ 

2, 2, 5, 5-tetramethyl hexane

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(b) 
$$+ Br_2 \xrightarrow{Heat} + HBr$$

33. (a) (i) On adding I<sub>2</sub> and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.

(ii) Phenol gives a violet colouration with FeCl<sub>3</sub> solution while ethanol does not.

$$3C_6H_5OH + FeCl_3 \longrightarrow (C_6H_5O)_3Fe + 3HCl$$
  
Phenol Violet colouration

#### C<sub>2</sub>H<sub>5</sub>OH + FeCl<sub>3</sub> → No violet colouration Ethanol

(b) Electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion by dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group is an electron donating group. Methoxy group destabilises the phenoxide ion by intensifying the negative charge. Thus, o-nitrophenol is more acidic than o-methoxyphenol.

34. (i) 
$$Na_2Cr_2O_7/H_2SO_4$$
Oxidation

Benzoquinone

OH

OH

OH

CH<sub>3</sub>-C-CH<sub>3</sub>+CH<sub>3</sub>MgBr

OH

CH<sub>3</sub>-C-CH<sub>3</sub>

CH<sub>3</sub>

CH<sub>3</sub>

CH<sub>3</sub>

2-Methylpropan-2-ol

OH

(iii) CH<sub>3</sub>CH=CH<sub>2</sub>

H<sub>2</sub>SO<sub>4</sub>

Propan-2-ol

OH

Propan-2-ol

35. (a) The phenoxide ion formed after loss of proton from phenol is resonance stabilised and thus, phenol loses H<sup>+</sup> ion to show acidic character.

On the other hand, alkoxide ion formed from hexanol shows no such resonance stabilisation and is unstable.

(b) In substituted phenols, the presence of electron releasing group decreases the acidic strength of phenol. This effect is more pronounced when such a group is present at *ortho* and *para*-positions. It is due to the increased negative charge in phenoxide ion. Thus *m*-aminophenol is stronger acid than *o*-aminophenol.

#### (c) (i) Zinc dust

(ii) Alkyl halide in the presence of anhydrous aluminium chloride, CH<sub>3</sub>Cl and AlCl<sub>3</sub> (anhy.)

(iii) Cu/573 K

OH
$$CH_{3}-CH-CH_{2}-CH_{3}\xrightarrow{CrO_{3}}CH_{3}-C-CH_{2}CH_{3}$$
Butan-2-ol
Butan-2-one

OH
$$CH_{3}-CH-CH_{2}-CH_{3}\xrightarrow{SOCl_{2}}$$
Butan-2-ol
$$CH_{3}-CH-CH_{2}-CH_{3}\xrightarrow{CH_{3}-CH-CH_{2}-CH_{3}}$$

(ii) Propan-1-ol on treatment with conc. H<sub>2</sub>SO<sub>4</sub> at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.

2-Chlorobutane

$$2CH_{3}-CH_{2}-CH_{2}-OH+H_{2}SO_{4} \xrightarrow{413 \text{ K}}$$

$$Propan-1-ol$$

$$CH_{3}-CH_{2}-CH_{2}-O-CH_{2}-CH_{2}-CH_{3}$$

$$1-Propoxypropane$$

Mechanism:

$$CH_3-CH_2-CH_2-OH+H^+$$

Propan-1-ol

 $CH_3-CH_2-CH_2-\dot{O}-H$ 

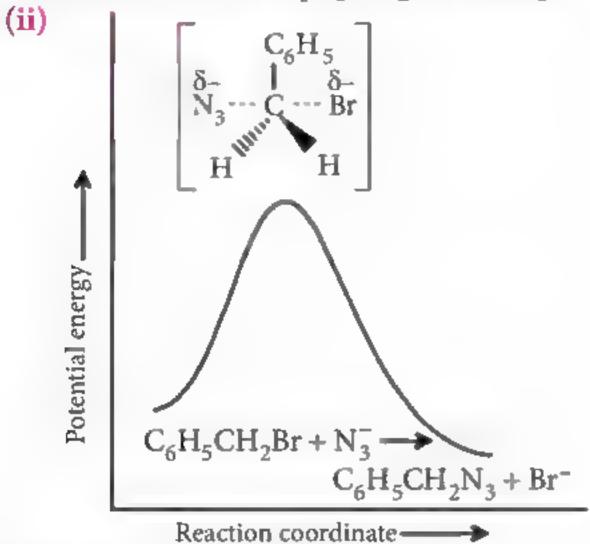
$$CH_{3}-CH_{2}-CH_{2}-\overset{\dagger}{O}-H \Longrightarrow$$

$$CH_{3}-CH_{2}-\overset{\dagger}{C}H_{2}+H_{2}O$$

$$CH_{3}-CH_{2}-CH_{2}-\overset{\dagger}{O}-H+CH_{3}-CH_{2}-\overset{\dagger}{C}H_{2}$$

$$CH_{3}-CH_{2}-CH_{2}-O-CH_{2}-CH_{2}-CH_{3}-\overset{\dagger}{C}H_{2}$$

**36.** (a) (i) Rate =  $k[C_6H_5CH_2Br]$  [NaN<sub>3</sub>]



(iii) The rate will be doubled.

(b) n-butyl bromide will give  $S_N^2$  reaction:

37. (a) In alcohols, -OH group is attached to electron releasing alkyl group which decreases polarity of O - H bond while in phenols -OH group is attached to electron withdrawing phenyl group which increases polarity of O - H bond.

(c) Aspirin is acetyl salicylic acid which is an analgesic used in pain relieving.

OR

Ethanol

(c) Formation of ethene:

Br

(c) Formation of ethene:

$$\xrightarrow{\text{aq. KOH}} \text{CH}_3 - \text{CH} - \text{CH}_3$$

$$\downarrow \text{OH}$$

$$\downarrow \text{OH}$$

$$\downarrow \text{OH}$$

$$\downarrow \text{OH}$$

$$\downarrow \text{H}$$

$$\downarrow \text{H}$$

$$\downarrow \text{Ethene}$$

$$\downarrow \text{Ethene}$$

Ethyl carbocation

(c) Phenols undergo electrophilic substitution reaction more easily than benzene due to strong activating effect of -OH group attached to benzene ring.

# MONTHLY TEST DRIVE MONTHLY TEST MONTHLY TE

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Total Marks: 120

#### BIOMOLECULES | POLYMERS | CHEMISTRY IN EVERYDAY LIFE

Time Taken: 60 Min.

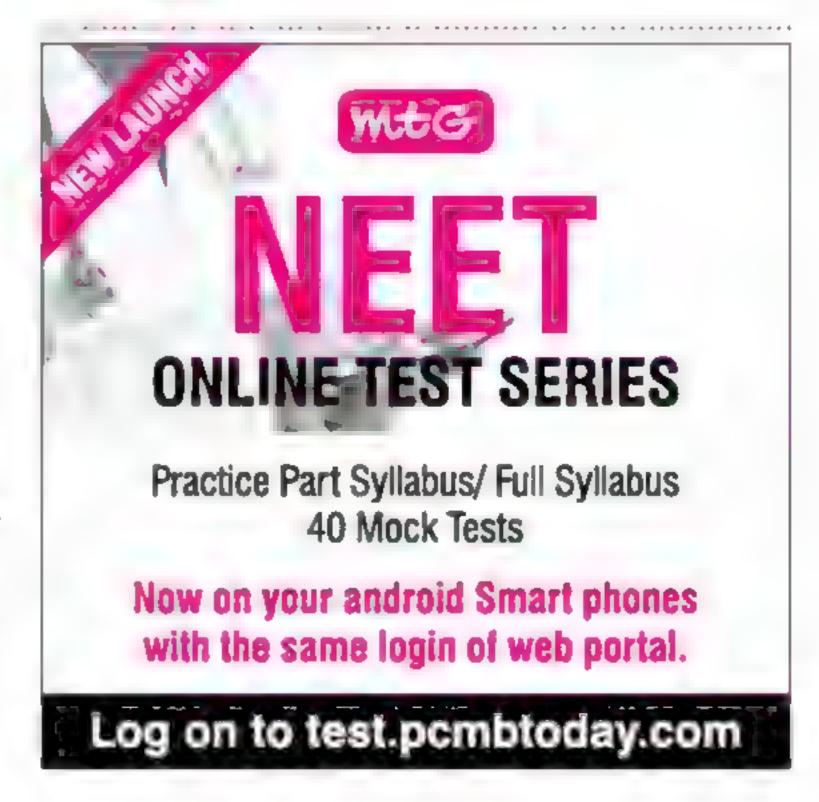
#### ® NEET# AIIMS

#### **Only One Option Correct Type**

- 1. Which of the following hexoses will form the same osazone when treated with excess of phenylhydrazine?
  - (a) D-glucose, D-fructose and D-galactose
  - (b) D-glucose, D-fructose and D-mannose
  - (c) D-glucose, D-mannose and D- galactose
  - (d) D-fructose, D-mannose and D-galactose
- 2. Which of the following gives paracetamol on acetylation?

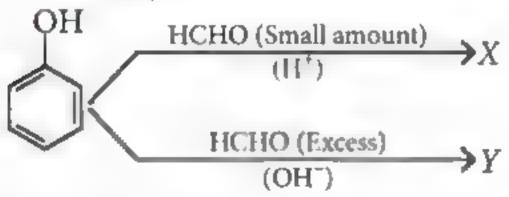
- 3. Novolac, the linear polymer used in paints is
  - (a) copolymer of 1, 3-butadiene and styrene
  - (b) obtained by the polymerization of methyl methacrylate
  - (c) initial product obtained in the condensation of phenol and formaldehyde in the presence of acid or base catalyst
  - (d) obtained by the polymerization of caprolactam
- 4. Polyvinyl alcohol can be prepared by
  - (a) polymerisation of vinyl alcohol
  - (b) alkaline hydrolysis of polyvinyl acetate

- (c) polymerisation of acetylene
- (d) reaction of acetylene with H<sub>2</sub>SO<sub>4</sub> in presence of HgSO<sub>4</sub>.
- 5. The reagent which may be used to distinguish between cane sugar and glucose solution is
  - (a) Molisch's reagent (b)
- (b) iodine solution
  - (c) Baeyer's reagent
- (d) Fehling's solution.
- Sodium metabisulphite is used in preserving squashes and other mildly acidic foods because
  - (a) potassium salt has preservative action
  - (b) sulphur dioxide and sulphurous acid formed kill bacteria and germs
  - (c) potassium metabisulphite prevents oxidation
  - (d) potassium metabisulphite is not influenced by acid.



- In both DNA and RNA, heterocyclic base and phosphate ester linkages are at
  - (a) C-5' and C-2' respectively of the sugar molecule
  - (b) C-2' and C-5' respectively of the sugar molecule
  - (c) C-1' and C-5' respectively of the sugar molecule
  - (d) C-5' and C-1' respectively of the sugar molecule.
- Which of the following alkenes is most reactive towards cationic polymerization?
  - (a)  $CH_2 = CHCH_3$  (b)  $H_2C = CHCl$

  - (c)  $H_2C = CHC_6H_5$  (d)  $H_2C = CHCO_2CH_3$
- Phenol gives two polymers on condensation with formaldehyde:



X and Y are

$\boldsymbol{X}$	$\boldsymbol{Y}$
(a) bakelite	novolac
(b) novolac	bakelite
(c) bakelite	bakelite
(d) novolac	novolac.

- 10. Pick out the statement which is not true?
  - (a) Tetrazine is harmful edible colour.
  - (b) Alitame is an artificial sweetener.
  - (c) Sodium alkyl sulphate is a cationic detergent.
  - (d) BHT is an antioxidant.
- 11. Cheilosis and digestive disorders are due to the deficiency of
  - (a) ascorbic acid
- (b) pyridoxine
- (c) thiamine
- (d) riboflavin.
- 12. The role of phosphate in detergent powder is to
  - (a) control pH level of the detergent water mixture
    - (b) remove Ca<sup>2+</sup> and Mg<sup>2+</sup> ions from the water that cause the hardness of water
    - (c) provide whiteness to the fabrics
  - (d) form solid detergents as phosphateless detergents are liquid in nature.

#### Assertion & Reason Type

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 13. Assertion : Alpha (α-) amino acids exist as internal salt in solution as they have amino and carboxylic acid groups in near vicinity.

Reason: H<sup>+</sup> ion given by carboxylic (-COOH) group is captured by amino (-NH<sub>2</sub>) group having lone pair of electrons.

14. Assertion: Polyamides are best used as fibres because of high tensile strength.

Reason: Strong intermolecular forces (like hydrogen bonding within polyamides) lead to close packing of chains and increase the crystalline character, hence, provide high tensile strength to polymers.

15. Assertion: The —As=As— linkage present in arsphenamine (a sulpha drug) resembles the —N=N—linkage present in azo dyes.

Reason: The first antibacterial agent, prontosil resembles in structure to the compound salvarsan.

#### JEE MAIN / ADVANCED 🗈

#### Only One Option Correct Type

- 16. The most important contribution to the stability of a protein conformation appears to be the
  - (a) entropy increase from the decrease in ordered water molecules forming a solvent shell around



- (b) maximum entropy increase from ionic interactions between the ionized amino acids in a protein
- (c) sum of free energies of formation of many weak interactions between its polar amino acids and surrounding water molecules
- (d) sum of free energies of formation of many weak interactions among the hundreds of amino acids in a protein.
- 17. Antiseptic chloroxylenol is
  - (a) 4-chloro-3, 5-dimethylphenol
  - (b) 3-chloro-4, 5-dimethylphenol
  - (c) 4-chloro-2, 5-dimethylphenol
  - (d) 5-chloro-3, 4-dimethylphenol
- 18. Which of the following monomers on polymerization give polyoxymethylene also known as polyacetal and which does not exist in isotactic, syndiotactic and atactic forms?
  - (a) Methoxyethene
- (b) Formaldehyde
- (c) Ethoxyethene
- (d) Propene
- 19. The segment of DNA which acts as the instruction manual for the synthesis of protein is
  - (a) ribose
- (b) gene
- (c) nucleoside
- (d) nucleotide.

#### More than One Options Correct Type

20. The correct statement(s) about the following sugar X and Y is (are)

- (a) X is a reducing sugar and Y is a non-reducing sugar
- (b) X is a non-reducing sugar and Y is a reducing sugar
- (c) the glycosidic linkage in X and Y are  $\alpha$  and  $\beta$  respectively
- (d) the glycosidic linkage in X and Y are  $\beta$  and  $\alpha$  respectively.

- 21. Which of the following statements are correct about barbiturates?
  - (a) Hypnotics or sleep producing agents.
  - (b) These are tranquilizers.
  - (c) Non-narcotic analgesics.
  - (d) Pain reducing without disturbing the nervous system.
- 22. Identify the incorrect statement.
  - (a) The starting material for the manufacture of PVC is obtained by reacting HCl with acetylene.
  - (b) Natural rubber is a step growth polymer.
  - (c) Dacron is addition polymer.
  - (d) Intermolecular forces present in nylon-6, 6 is H-bonding.
- 23. The correct statements about anomers are
  - (a) Anomers have different stereochemistry at C-1 (anomeric carbon)
  - (b) α-D-glucopyranose and β-D-glucopyranose are anomers
  - (c) Both anomers of D-glucopyranose can be crystallised and purified.
  - (d) When pure α-D-glucopyranose is dissolved in water its optical rotation slowly changes



#### Numerical Value Type

- 24. Total number of lone pairs of electrons in melamine is
- 25. The substituents  $R_1$  and  $R_2$  for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH 7.0?

$$H_3N$$
- $\overset{+}{C}H$ - $CO$ - $NH$ - $CH$ - $CO$ - $NH$ - $CH$ - $CONH$ - $CH$ - $COO$ - $H$ - $H$ - $R_1$   $R_2$   $H$ 

Peptide	$R_1$	$R_2$
I	Н	Н
II	Н	CH <sub>3</sub>
III	CH <sub>2</sub> COOH	Н
IV	CH <sub>2</sub> CONH <sub>2</sub>	(CH2)4NH2
V	CH <sub>2</sub> CONH <sub>2</sub>	CH <sub>2</sub> CONH <sub>2</sub>
VI	(CH2)4NH2	(CH2)4NH2
VII	CH <sub>2</sub> COOH	CH <sub>2</sub> CONH <sub>2</sub>
VIII	CH <sub>2</sub> OH	(CH2)4NH2
IX	(CH2)4NH2	CH <sub>3</sub>

26. The maximum number of neurologically active drugs amongst the following are: Iproniazid, phenelzine, chlordiazepoxide, meprobamate, diclofenac sodium, ibuprofen, naproxen, seconal, paracetamol.

#### Matrix Match Type

Answer the following questions (27 and 28) by appropriately matching the columns based on the information given in the passage:

Polynucleotides are called nucleic acids. Each nucleotide is made up of three parts, i.e., a pentose sugar, a heterocyclic nitrogenous base and phosphoric acid. Depending upon the nature of sugar whether, ribose or 2-deoxyribose, nucleic acids are called RNA and DNA respectively. In all, there are five nitrogenous bases, two of which are purines while the remaining three are pyrimidines. Out of these five bases, each types of nucleic acid has four of them.

	Column-I	Column-II		
A.	Adenine	P.	Purine	
B.	Thymine	Q.	Pyrimidine	
C.	Uracil	R.	RNA	
D.	Ribose	S.	DNA	

- 27. Which of the following has the correct combination considering Column-I and Column-II?

  - (a)  $A \rightarrow P, Q$  (b)  $B \rightarrow Q, S$

  - (c)  $C \rightarrow P, R$  (d)  $D \rightarrow Q, P$
- 28. Which of the following has the correct combination considering Column-I and Column-II?

  - (a)  $A \rightarrow P, R, S$  (b)  $B \rightarrow Q, R, S$
  - (c)  $C \rightarrow P$ , Q, S (d)  $D \rightarrow P$ , Q, R

Answer the following questions (29 and 30) by appropriately matching the columns based on the information given in the passage:

Drugs designed to cure some ailment in one organ in the body do not affect the other because they work on different receptors. For example, secretion of histamine causes allergy. It also causes acidity due to release of hydrochloric acid in the stomach. Since antiallergic and antacids drugs work on different receptors therefore, antiallergic dugs remove allergy while antacids remove acidity.

Column-I		Column-II		
A.	Adrenaline	P.	Releases HCl from stomach walls	
B.	Noradrenaline	Q.	Causes allergy	
C.	Histamine	R.	Hormone	
D.	Dopamine	S.	Neurotransmitter	

- 29. Which of the following has the correct combination considering Column-I and Column-II?
  - (a)  $A \rightarrow P, S$
- (b)  $B \rightarrow P, Q, S$
- (c)  $C \rightarrow P$ , Q, R, S (d)  $D \rightarrow Q$ , R
- 30. Which of the following has the correct combination considering Column-I and Column-II?
  - (a)  $A \rightarrow R$ , S, P
- (b)  $B \rightarrow R$ , S
- (c)  $C \rightarrow P, R$
- (d)  $D \rightarrow P_1 Q_1 R$



Keys are published in this issue. Search now!



Marks scored in percentage .....

No. of questions attempted

No. of questions correct

#### Check your score! If your score is

> 90% EXCELLENT WORK! You are well prepared to take the challenge of final exam.

90-75% GOOD WORK! 74-60% SATISFACTORY!

You can score good in the final exam. You need to score more next time.

< 60% NOT SATISFACTORY! Revise thoroughly and strengthen your concepts.

# CHEMISTRY MUSING

**PROBLEM SET 75** 

hemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIMS / JIPMER with additional study material. In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue. We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

#### JEE MAIN/NEET

- 1. A mixture containing 1.12 L of D<sub>2</sub> and 2.24 L of H<sub>2</sub> at NTP is taken inside a bulb connected to another bulb through a stopcock with a small opening. The second bulb is fully evacuated. The stopcock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D<sub>2</sub>. Concentration (% by mass) of the gases in second bulb is
  - (a)  $D_2 = 41.66\%$ ,  $H_2 = 58.33\%$
  - (b)  $D_2 = 58.33\%$ ,  $H_2 = 41.66\%$
  - (c)  $D_2 = 50\%$ ,  $H_2 = 50\%$
  - (d)  $D_2 = 60\%$ ,  $H_2 = 40\%$
- 2. In the reaction with Tollens' reagent acetylene shows
  - (a) oxidising property (b) reducing property

  - (c) basic property (d) acidic property.
- 3. At 627°C and one atmosphere pressure SO<sub>3</sub> is partially dissociated into SO2 and O2 as

$$SO_{3(g)} \Longrightarrow SO_{2(g)} + \frac{1}{2}O_{2(g)}$$
. The density of the

equilibrium mixture is 0.925 g/litre. Its degree of dissociation is

- (a) 32.20% (b) 30.21% (c) 36.20% (d) 34.08%
- 4. Surface catalysed reactions that are inhibited by the products obey the rate equation (in some cases),  $\frac{dx}{dt} = \frac{K(a-x)}{1+x^2}$ , where a is the initial concentration of the reactant and K and b are constants. If x is the concentration of products at any time t and the reaction is  $A \longrightarrow B$ , then  $t_{1/2}$  may be calculated by

(a) 
$$\frac{\log 2 + ab(\log 2 - 0.5)}{K}$$

(b) 
$$\frac{ab(\log 2 - 0.5)}{\log 2 \times K}$$
 (c)  $\frac{\log 2 \times K}{ab(\log 2 - 0.5)}$ 

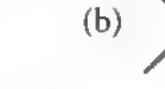
(d) 
$$\frac{K}{\log 2 + ab(\log 2 - 0.5)}$$

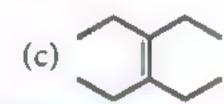
- When methyl D-glucopyranoside is oxidized with periodic acid, how many moles of the oxidizing agent are consumed per mole of the sugar?
  - (a) 2
- (b) 3
- (c) 4

#### JEE ADVANCED

Identify X for the given reaction.

$$X \xrightarrow{1. O_3/Zn-H_2O} CH_3CH_2CH_2CO_2CH_3$$





#### COMPREHENSION

The conversion of an amide into an amine with one carbon atom less by the action of bromine in sodium hydroxide is known as Hofmann bromamide degradation reaction.

$$RCONH_2 \xrightarrow{Br_2/NaOH} R-NH_2$$

The most important feature of the reaction is the rearrangement of N-bromamide anion to isocyanate.

$$R - C - NH_2 \xrightarrow[\overline{OH}]{Br_2} R - C - N \xrightarrow[Step 1]{H} \xrightarrow[\overline{OH}]{OH}$$

$$R - C - NH_2 \xrightarrow[\overline{OH}]{Br} \xrightarrow[Step 2]{H} \xrightarrow[Step 1]{OH}$$

$$R - \stackrel{\circ}{C} - \stackrel{\circ}{\stackrel{\circ}{N}} - \stackrel{\circ}{\stackrel{\circ}{\text{Br}}} \xrightarrow{R} - \stackrel{\circ}{\stackrel{\circ}{\text{N}}} = C = O$$

$$\stackrel{\circ}{\stackrel{\circ}{\text{OH}}} \stackrel{\circ}{\stackrel{\circ}{\text{H}_2}} O$$

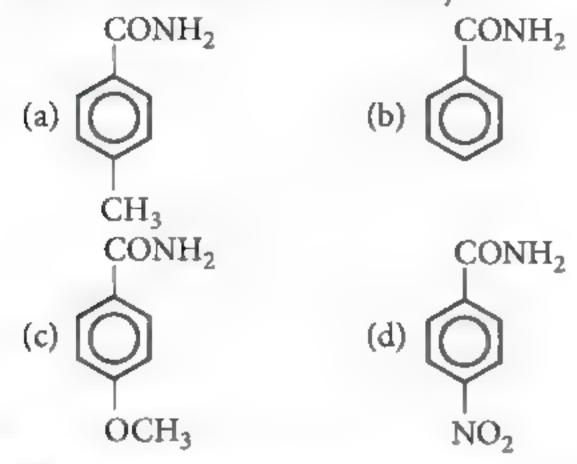
$$R - N \stackrel{\circ}{\text{H}_2} O$$

7. The product of the following reaction will be

$$C_6H_5 \xrightarrow{H} CONH_2 \xrightarrow{Br_2/KOH} CH_3$$

- (a) S-amine
- (b) R-amine
- (c) 50:50 mixture of (+) and (-) amine
- (d) 30:70 mixture of (+) and (-) amine.

8. Which of the following can undergo Hofmann bromamide reaction most easily?



#### NUMERICAL VALUE

- 9. A certain dye absorbs light of  $\lambda = 4530$  Å and then emits fluorescence light of 5080 Å. Assuming that under given conditions 47% of the absorbed energy is re-emitted out as fluorescence, the ratio of no. of quanta emitted out to the no. of quanta absorbed is found to be  $x \times 10^{-2}$ . What is the value of x?
- 10. 0.535 g ethanol and acetaldehyde mixture when heated with Fehling's solution gave 1.2 g of a red precipitate. What is the percentage of acetaldehyde in the mixture? (At. wt. of Cu = 63.54).





#### **JOINT ENTRANCE EXAMINATION MAIN - 2020**

The National Testing Agency (NTA) will conduct the JEE Main-2020 Examination twice for admission to Undergraduate Programs in NITs, IIITs and other Centrally Funded Technical Institutions (CFTIs), etc. in the next academic year (2020-2021). The First JEE Main-2020 will be conducted in January 2020 between 6<sup>th</sup> January (Monday) and 11<sup>th</sup> January (Saturday) 2020 and the Second JEE Main-2020 will be conducted between 3<sup>rd</sup> April (Thursday) 2020.

As per the eligibility criteria for B.Arch and B Planning courses and according to the opinion of Subject Experts, a few changes in the pattern of the question paper(s) and number of question(s) for B.E./B.Tech, B.Arch and B.Planning have been approved by the JEE Apex Board (JAB) for the conduct of JEE Main-2020 Examination.

The pattern of question paper(s) is given below:

PAPER	SUBJECTS	NO. OF	TYPE OF QUESTIONS	TIMING OF THE EXAMINATION(IST)		
		QUESTIONS		First Shift	Second Shift	
	Mathematics	25(20+5)	20 Objective Type - Multiple Choice Questions (MCQs) &	09.30 a.m	02.30 p.m.	
B.E./B.Tech.	Physics	25(20+5)	5 Questions with answer as numerical value, with equal	to	to	
	Chemistry	25(20+5)	we ghtage to Mathematics, Physics & Chemistry	12:30 p.m	05:30 p m	
0.4	Mathematics – Part I	25(20+5)	20 Objective Type - Multiple Choice Questions (MCQs) & 5 Questions for which answer is a numerical value	09:30 a m to 12:30 p.m.	02:30 p m to 05:30 p.m.	
B. Arch.	Aptitude Test — Part II	50	Objective Type - Multiple Choice Questions (MCQs)			
	Drawing Test - Part III	2	Questions for drawing test			
B. Planning	Mathematics – Part I	25(20+5)	20 Objective Type - Multiple Choice Questions (MCQs) & 5 Questions for which answer is a numerical value			
	Aptitude Test - Part II	50	Objective Type - Multiple Choice Questions (MCQs)	02 30 p.m. to 05 30 p.m.		
	Planning Based Questions - Part III	25	Objective Type - Multiple Choice Questions (MCQs)			

The above Examinations will be held in "Computer Based Test" (CBT) Mode only, except that the Drawing Test for B Arch, will be held in "Pen & Paper" (offline) mode. A candidate may appear in B.E./B.Tech, B.Arch and B.Planning depending upon the course/s he/she wishes to pursue.

The candidates aspiring to take admission to the undergraduate programs at IITs for the year 2020 will also have to appear in B. E. /B. Tech. Paper of JEE Main -2020. Based on the performance in the B.E./B. Tech. of JEE Main-2020, number of top candidates as per the requirement for JEE Advanced-2020 will be eligible to appear in JEE Advanced-2020. Admission to IITs will be based on category -wise All India Rank (A R) in JEE Advanced, subject to the conditions as would be mentioned in JEE Advanced-2020 website.

For the April JEE Main-2020, a separate notice will be issued later on and the candidates will be required to apply separately. However, candidates are not required to compulsorily appear in both the tests it eligibility of JEE Main-2020 and April JEE Main-2020. In case, a candidate appears in both the tests, the better of the two scores will be used for the admissions and eligibility of JEE Advanced-2020.

For more information visit www.jeemain.nic.in



Hello, My stars over there!! Wish you a very HAPPY DURGA PUJA & DUSSEHRA at first. Festive season is coming. Be safe and be helpful. Don't forget just after the festive month, the EXAM SEASON will be knocking at the door. So keep your eyes at your aim. You still have some time to learn in depth concept. So do that. As always I am there to help you. This article will help you grasp idea about a fantastic concept in thermodynamics. More to come in near future. Take care! All the best.

\*Arunava Sarkar

#### Common Points to Take Care in Thermodynamics

We all know what is Gibbs-Helmholtz relation. It is

 $\Delta G = \Delta H + T \left[ \frac{d}{dT} (\Delta G) \right]$ 

We are very much accustomed to predict the spontaneity of a reaction based on the value of  $\Delta G$ . Also we can calculate the value of  $\Delta H$  if we know  $\Delta G$  and its variation with temperature. Now, have you ever thought that if you calculate  $\Delta H$  calorimetrically or otherwise then can you ascertain  $\Delta G$ ? Answer is 'No'. The big reason for this is  $\frac{d}{dT}(\Delta G)$  can't be properly ascertained. The

reason is as below.

$$\Delta G = \Delta H + T \left[ \frac{d}{dT} (\Delta G) \right]_{p}$$

$$\Rightarrow \left[ \frac{d}{dT} (\Delta G) \right]_{p} = \left[ \frac{d}{dT} (\Delta H) \right]_{p}$$

$$+ T \left[ \frac{d^{2} (\Delta G)}{dT^{2}} \right]_{p} + \left[ \frac{d}{dT} (\Delta G) \right]_{p}$$

$$\Rightarrow \left[ \frac{d^{2} (\Delta G)}{dT^{2}} \right]_{p} = -\frac{1}{T} \left[ \frac{d}{dT} (\Delta H) \right]_{p} \qquad ...(1)$$

$$\Rightarrow \left[ \frac{d^{2} (\Delta G)}{dT^{2}} \right]_{p} = -\frac{1}{T} P \cdot \sum_{i} V_{i} \ \overline{C}_{P_{i}} \qquad ...(2)$$

Here,  $V_i$  is the stoichiometric co-efficient for  $i^{th}$ constituent. It is found to be negative for the reactant and positive for the product. Now, integrating equation (2) from absolute zero to temperature T.

From equation (2),

$$\int_{0}^{T} \frac{d^{2}(\Delta G)}{dT^{2}} dT = -\int_{0}^{T} \frac{1}{T} \sum V_{i} \overrightarrow{C}_{P_{i}} dT$$

$$\Rightarrow \left[ \frac{d}{dT} (\Delta G) \right]_{T} = -\int_{0}^{T} \frac{1}{T} \sum V_{i} \overrightarrow{C}_{P_{i}} dT + \left[ \frac{d}{dT} (\Delta G) \right]_{T=0}$$
...(3)

In eqn. (3), the first term in the right hand side can easily be calculated as the variation of  $\overline{C}_P$  is known with temperature. But, the value of second term cannot be calculated.

So, 
$$\left[\frac{d}{dT}(\Delta G)\right]_T$$
 can't be known.

Hence, from a knowledge of  $\Delta H$  at any given temperature,  $\Delta G$  can't be known.

Monthly Test Drive CLASS XII WANSWER

1.	(b)	2.	(c)	3.	(c)	<b>4.</b> (b)
5.	(d)	6.	(b)	7.	(c)	8. (c)
9.	(b)	10.	(c)	11.	(d)	<b>12.</b> (b)
13.	(a)	14.	(a)	15.	(b)	16. (a)
17.	(a)	18.	(b)	19.	(b)	<b>20.</b> (b,c)
21.	(a,b)	22.	(a,b,c)	23.	(a,b,c,d)	<b>24.</b> (6)
25.	(4)	26.	(9)	27.	(b)	<b>28.</b> (a)
29.	(c)	<b>30.</b>	(b)			

<sup>\*</sup>Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

The solution to this problem was given by Nernst as it is known as Nernst Heat Theorem and this is also the precursor of third law of thermodynamics enunciated by Planck's in 1912.

#### **NERNST HEAT THEOREM**

According to Gibbs-Helmholtz equation, for a reaction at T = 0,  $\Delta G = \Delta H$ . This is because at T = 0,  $T\left[\frac{d}{dT}(\Delta G)\right] = 0$ , where  $\frac{d}{dT}(\Delta G)$  may or may not

be equal to zero.

Actually, with the lowering in temperature  $\Delta G$  and  $\Delta H$  approach each other rapidly. *i.e.*, when  $T \rightarrow 0$ ,  $\Delta G = \Delta H$ . In 1906, Nernst told that for a process in a condensed

system 
$$\left[\frac{d}{dT}(\Delta G)\right]$$
 will be zero at the vicinity of

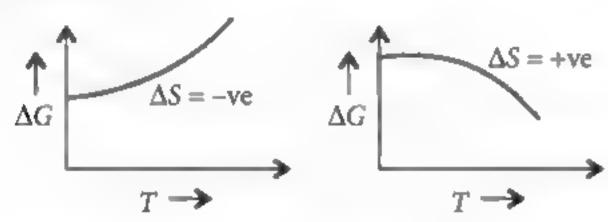
absolute zero.

So, 
$$\lim_{T\to 0} \left[ \frac{d}{dT} (\Delta G) \right]_P = 0$$

This was indeed a bold postulate.

We know, 
$$\frac{d}{dT}(\Delta G) = -\Delta S$$

Entropy is a function of temperature. As  $\Delta S$  of a reaction can be positive or negative, therefore,  $\Delta G$  of a reaction may decrease or increase with lowering of temperature *i.e.*,



 $\Delta H$  can also vary with temperature as  $\frac{d}{dT}(\Delta H) = \Delta C_P$  and  $C_P$  is a function of temperature.

According to Nernst heat theorem, at absolute zero  $\Delta G = \Delta H$  and near the zone of absolute zero,  $\Delta H$  approaches asymptotically to  $\Delta G$ . So,  $\lim_{T\to 0} \frac{d}{dT}(\Delta H) = 0$  So, overall,

$$\operatorname{Lim}_{T\to 0} \frac{d}{dT} (\Delta G) = 0, \operatorname{Lim}_{T\to 0} \frac{d}{dT} (\Delta H) = 0$$
Now,  $\Delta G - \Delta H = T \frac{d}{dT} (\Delta G)$ 

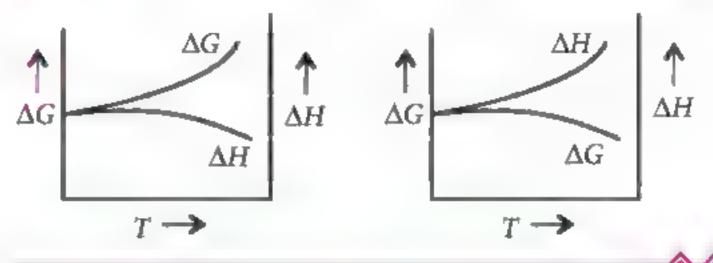
$$\Rightarrow \frac{d}{dT} (\Delta G) - \frac{d}{dT} (\Delta H) = \frac{d}{dT} (\Delta G) + T \frac{d^2}{dT^2} (\Delta G)$$

$$\Rightarrow -\frac{d}{dT} (\Delta H) = T \cdot \frac{d^2 (\Delta G)}{dT^2}$$

Now,  $\Delta G$  converges to limiting value at T=0. So,

$$T\frac{d^2}{dT}(\Delta G)$$
 and  $\frac{d}{dT}(\Delta G)$  will have the same sign.

Therefore,  $\frac{d}{dT}(\Delta H)$  and  $\frac{d}{dT}(\Delta G)$  have opposite sign.





## Water harvester makes it easy to quench your thirst in the desert

To deal with water scarcity a major problem worldwide, researchers are close to producing a microwave-sized water harvester that will allow you to pull all the water you need directly from the air even in the hot, dry desert.

Scientists describe the latest version of their water harvester, which can pull more than five cups of water (1.3 litres) from low-humidity air per day for each kilogram (2.2 pounds) of water-absorbing material, a very porous substance called a metal-organic framework, or MOF. That is more than the minimum required to stay alive.

A new MOF design could rapidly adsorb water from even dry air, allowing it to be condensed and collected for drinking. A second-generation MOF can now cycle through adsorption and desorption in 20 minutes, allowing continuous collection of more than a litre per day per kilogram of MOF using solar power.

The harvester cycles 24/7, powered by solar panels and a battery. "It is well known that in order to condense water from air at a low humidity (less than 40 percent relative humidity) you need to cool down the air to below freezing, to zero degrees Celsius, which is impractical. With our harvester, we are doing this at very low humidity without such cooling; there is no other material that can do that," said scientist. "This is not like a dehumidifier, which operates at high relative humidity. Some people say that 0.7 litres is not a lot of water. But it is a lot of water, if you don't have water." An even larger version of the harvester, one the size of a small refrigerator, will provide 200 to 250 litres of water per day, enough for a household to drink, cook and shower. And in a couple of years, the company hopes to have a village-scale harvester that will produce 20,000 litres per day. All would run on power from solar panels and a battery or off the electrical grid.



#### Dear Readers,

We have been receiving a lot of queries from students and their parents, so we decided to ease you out by introducing a new column to guide you through your worries, concerns and questions related to your studies and beyond. Readers can send their queries (concerns beyond specific subjects, career guidance, tips for better performance, etc.) by post or by email at editor@mtg.in. The solutions to your queries given by MTG experts will definitely ease your anxiety and provide you a clear vision and a right direction to achieve your goals. Best and most relevant questions will be chosen and published with the sender's name.

V I am a student of class 12<sup>th</sup>, aspiring to pursue higher studies in the field of astronomy. However, I am really confused about the correct pathway. What shall I need to do? I am also interested in robotics and manufacturing engineering. I seek career guidance.

(Tithi Bose, Kolkata, West bengal)

It is good that you are thinking to opt for unique career options. We would like to tell you that 'astronomy' is an observational science rather than a experimental one. Astronomers implement the principles of mathematics and physics to carry out research about the universe.

Astronomy and Astrophysics both the terms are used to refer the same subject. Astronomy is the science of measuring the positions & characteristics of heavenly bodies and astrophysics is the application of physics to understand astronomy. You may join the undergraduate course followed by postgraduate course.

Note: Ph.D. is compulsory to become an astronomer.

You may opt from below mentioned courses after 10 + 2 (Science stream):

#### Bachelor's courses

- B.Sc. in Astrophysics
- ➤ B.Sc. in Astronomy
- ➤ B.Tech. in Electronics and Communication or Electrical Engineering

#### Master's courses

- M.Sc. in Astronomy
- M.Tech. in Astronomy and Space Engineering

#### Doctoral courses

Ph.D. in Astronomy/Astrophysics/Atmospheric Sciences

#### Now about Robotics:

Two common professions that you can choose in robotics are:

(i) Robotics technicians (ii) Robotics engineers

#### Robotics Technicians

2 years associate degree in Robotics Technology

#### Robotics Engineer

- ➤ B.Tech. in Robotics Engineering
- ▶ B.Tech. in Automation Engineering
- ▶ B.Tech. in Mechatronics
- Bachelor of Engineering in Advanced Robotics

V My percentage in 12<sup>th</sup> is 69% having maths, and biology subjects. What will be the best courses for me to pursue? (Avantika Rai, Delhi)

There are many options for a science student. When you have more options, it is always difficult to choose. So, don't get confused, choose wisely. Before choosing your stream, you should know your strengths, aptitude and most importantly, your interest.

Here is a list of courses you can opt for:

#### For Medical

- MBBS
- BDS-Dentistry
- BAMS-Ayurveda
- Biotechnology
- Radiography, etc.

#### For Engineering

- > Architecture
- Merchant Navy
- Nanotechnology
- Defense Engineering etc.

Other than medical and engineering, you can also opt for Travel and Tourism Management, Banking, Insurance Management Studies, etc.

V I am a student of class  $10^{th}$ . I am really confused about the stream, which I will have to choose in Class 11. How should I select the right option? (Kumkum, Rajasthan)

The stream that you will choose in Class 11<sup>th</sup>, will decide your future in the long run.

So, you must take decision wisely keeping in mind your interests, strengths and career options that you want to choose.

- Search the streams available
- Discuss with your parents and teachers.

  You just need to go according to your strengths

and put some extra efforts to make a successful career.

All the Best



with Numerical Value Type Questions

- The order of increasing acidic strength for boron hydride is
  - (a)  $B_5H_9 < B_6H_{10} < B_{10}H_{14}$
  - (b)  $B_{10}H_{14} < B_5H_9 < B_6H_{10}$
  - (c)  $B_6H_{10} < B_{10}H_{14} < B_5H_9$
  - (d)  $B_{10}H_{14} < B_6H_{10} < B_5H_9$
- Which of the following plots does not represent the behaviour of an ideal binary liquid solution of A and B?
  - (a) Plot of  $p_B$  vs  $X_B$  is linear.
  - (b) Plot of  $p_A$  vs  $X_A$  is linear.
  - (c) Plot of  $P_{\text{Total}}$  vs  $X_A$  or  $X_B$  is linear.
  - (d) None of these
- Consider the following reaction,

In an experiment, 1.99 g of bromide A on reaction with ethanolic potassium hydroxide gave 1.062 g of a mixture of the olefin B and C. If the ratio of olefins B:C formed is 2:1, the yield for their formation respectively are

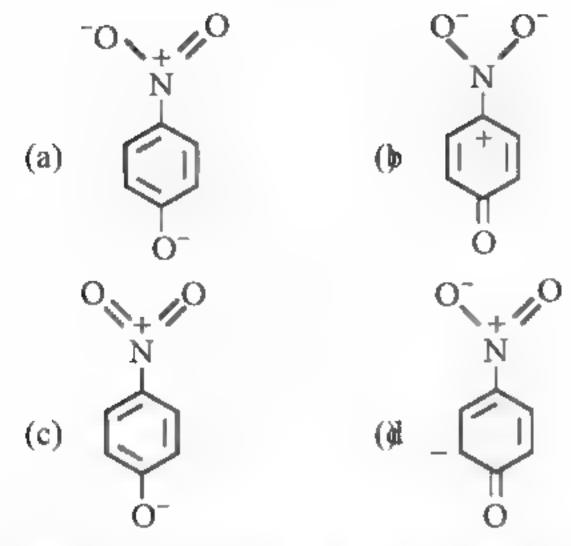
- (a) 60 and 30%
- (b) 50 and 25%
- (c) 66 and 33%
- (d) 54 and 27%
- 4. Red hot carbon will remove oxygen from the oxide AO and BO but not from MO, while B will remove oxygen from AO. The activity of metals A, B and M in decreasing order is
  - (a) A > B > M
- (b) B > A > M
- (c) M > B > A
- (d) M > A > B
- 5. For which of the following parameters, the structural isomers C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>OCH<sub>3</sub> would be expected to have the same values? (Assume ideal behaviour)
  - (a) Heat of vaporisation
  - (b) Vapour pressure at the same temperature
  - (c) Boiling points
  - (d) Gaseous densities at the same temperature and pressure

- Number of molecules in 100 mL of each of O<sub>2</sub>, NH<sub>3</sub> and CO<sub>2</sub> at STP are
  - (a) in the order  $CO_2 < O_2 < NH_3$
  - (b) in the order  $NH_3 < O_2 < CO_2$
  - (c) the same
  - (d) in the order  $NH_3 = CO_2 < O_2$
- A coordination complex compound of cobalt has molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three mole ions in an aqueous solution. On reacting this solution with excess of silver nitrate solutions, two moles of AgCl get precipitated. The ionic formula of this complex would be
  - (a)  $[Co(NH_3)_4(NO_2)Cl][(NH_3)Cl]$
  - (b)  $[Co(NH_3)_5Cl][Cl(NO_2)]$
  - (c)  $[Co(NH_3)_5(NO_2)]Cl_2$
  - (d)  $[Co(NH_3)_5][(NO_2)_2Cl_2]$

8. O 
$$\xrightarrow{\text{OH}} \xrightarrow{\text{Br}_2} A, A \text{ is}$$

(c) 
$$\bigcirc$$
 OH  $\bigcirc$  (d)  $\bigcirc$  Br

- Acyclic stereoisomers having the molecular isomers respectively are
  - formula, C<sub>4</sub>H<sub>7</sub>Cl, the geometrical and optical
  - (a) 6, 2
- (b) 4, 2
- (c) 6, 0
- (d) 4, 0
- 10. Silver is obtained from Na[Ag(CN)<sub>2</sub>] by reaction with
  - (a) Fe
- (b) Na
- (c) Zn
- (d) Au
- 11. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is



- 12. If the de Broglie wavelength of a particle of mass m is 100 times its velocity, then its value in terms of its mass (m) and Planck's constant (h) is
  - (a)  $\frac{1}{10}\sqrt{\frac{m}{h}}$  (b)  $10\sqrt{\frac{h}{m}}$  (c)  $\frac{1}{10}\sqrt{\frac{h}{m}}$  (d)  $10\sqrt{\frac{m}{h}}$
- 13. A soluble compound of a poisonous element M, when heated with Zn/H<sub>2</sub>SO<sub>4</sub> gives a colourless and extremely poisonous gaseous compound N, which on passing through a heated tube gives a silver mirror of element M, then M and N will be
  - (a) As and AsH<sub>3</sub>
- (b) P and PH<sub>3</sub>
- (c) N and NH<sub>3</sub> (d) Sb and SbH<sub>3</sub>
- 14. The pair of which salts is expected to have same colour in their freshly prepared aqueous solutions.
  - (a) VOCl<sub>2</sub>, CuCl<sub>2</sub>
- (b) CuCl<sub>2</sub>, FeCl<sub>2</sub>

  - (c) FeCl<sub>2</sub>,VOCl<sub>2</sub> (d) MnCl<sub>2</sub>, FeCl<sub>2</sub>
- 15. The Cahn-Ingold-Prelog (CIP) priorities of the group and the absolute configuration (R/S) of the following compound are

$$OH$$
 $CH = CH_3$ 
 $CH_3$ 

- (a)  $-CH_2OH > -CH(CH_3)_2 > -CH = CH_2 > -CH_3$ and S
- (b)  $-CH_2OH > -CH = CH_2 > -CH(CH_3)_2 > -CH_3$ and S
- (c)  $-CH_2OH > -CH = CH_2 > -CH(CH_3)_2 > -CH_3$ and R
- (d)  $-CH_2OH > -CH(CH_3)_2 > -CH = CH_2 > -CH_3$ and R.
- 16. After completion of the reactions (I and II), the organic compound(s) in the reaction mixtures is(are)

- (a) Reaction I: P and Reaction II: P
- (b) Reaction I: U, acetone and Reaction II: Q, acetone
- (c) Reaction I: T, U, acetone and Reaction II: P
- Reaction I: R, acetone and Reaction II: S, aceto
- Consider the following equation for a cell reaction

$$A + B \rightleftharpoons C + D$$
  $E^{\circ} = x \text{ V}, K_{eq} = K_1$   
 $2A + 2B \rightleftharpoons 2C + 2D$   $E^{\circ} = v \text{ V}, K_{eq} = K_2$ 

$$E^{\circ} = x \text{ V}, K_{eq} = K_1$$

$$2A + 2B \implies 2C + 2D$$
  $E^{\circ} = y \text{ V}, K_{eq}^{\circ q} = K_2$ 

$$E^{\circ} = y \text{ V}, K_{eq} = K_2$$

then

(a) 
$$x = y$$
;  $K_1 = \frac{1}{K_2}$  (b)  $x = y$ ;  $K_1 = K_2^2$ 

(b) 
$$x = y$$
;  $K_1 = K_2^2$ 

(c) 
$$x = y$$
;  $K_2 = K_1^2$  (d)  $x = 2y$ ;  $K_1 = 2K_2$ 

(d) 
$$x = 2y$$
;  $K_1 = 2K_2$ 

- 18. Out of  $N_2O$ ,  $SO_2$ ,  $I_3^+$ ,  $I_3^-$ ,  $H_2O$ ,  $NO_2^-$  and  $N_3^-$ , the linear species are
- (a)  $NO_2^-$ ,  $I_3^+$ ,  $H_2O$  (b)  $SO_2$ ,  $I_3^+$ ,  $N_3^-$  (c)  $N_2O$ ,  $I_3^-$ ,  $N_3^-$  (d)  $N_3^-$ ,  $I_3^+$ ,  $SO_2$
- 19. Graph between  $\log k$  and  $\frac{1}{T}$  is a straight line with OX = 5,  $\tan \theta = \left(\frac{1}{2.303}\right)$ . Hence,  $E_a$  will be
  - (a)  $2.303 \times 2$  cal
  - (b)  $\frac{5}{2.303}$  cal

1/T

- (c) -2 cal (d) none of these.
- 20. One mole of oxygen at 273 K and one mole of sulphur dioxide at 546 K are taken in two separate containers, then,
  - (a) kinetic energy of  $O_2$  > kinetic energy of  $SO_2$
  - (b) kinetic energy of  $O_2$  < kinetic energy of  $SO_2$
  - (c) kinetic energy of both are equal
  - (d) none of the above.

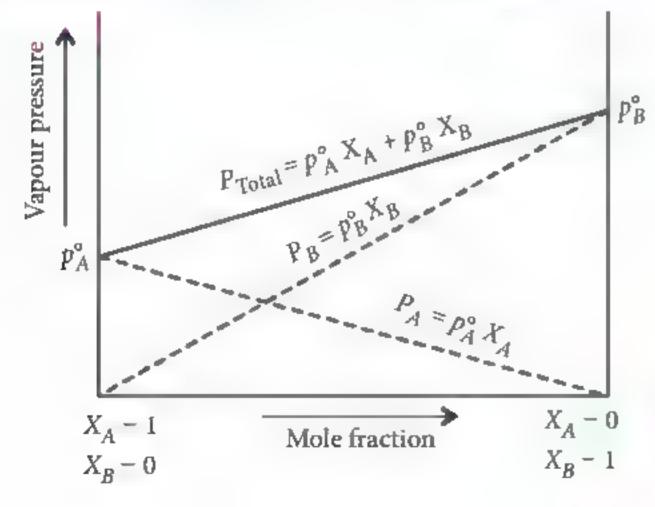
#### **Numerical Value Type**

- 21. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallises in cubic lattice. If the density is 2g/cc then find the radius of metal atom.  $(N_A = 6 \times 10^{23})$ . Give the answer in pm.
- 22. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K<sup>-1</sup>, the numerical value for the enthalpy of combustion of the gas in kJ mol<sup>-1</sup> is
- 23. The density of an equilibrium mixture of  $N_2O_4$  and  $NO_2$  at 1 atm and 348 K is 1.84 g dm<sup>-3</sup>. Calculate the equilibrium constant of the reaction  $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
- 24. All the energy released from the reaction  $X \to Y$ ,  $\Delta_r G^\circ = -193$  kJ mol<sup>-1</sup> is used for oxidizing  $M^+$  as  $M^+ \to M^{3+} + 2e^-$ ,  $E^\circ = -0.25$  V. Under standard conditions, the number of moles of  $M^+$  oxidized when one mole of X is converted to Y is [F = 6] [C] m [b] [F = 6]
- 25. A decapeptide (Mol. wt. 796) on complete hydrolysis gives glycine (Mol. wt. 75), alanine and phenylalanine. Glycine contributes 47.0% to the total weight of the hydrolysed products. The number of glycine units present in the decapeptide is

#### SOLUTIONS

- (a): Acidic strength of boranes 

  No. of B-atoms in the compound.
- 2. (c) : Plot of  $P_{\text{Total}}$  vs  $X_A + X_B$  is linear.



3. (a): 
$$(A)$$
Br
 $(B)$ 
 $(B)$ 
 $(C)$ 
 $(C)$ 
 $(B)$ 
 $(C)$ 
 $(C)$ 

M.wt. of  $A = 199 \text{ g mol}^{-1}$ M.wt. of B or  $C = 118 \text{ g mol}^{-1}$ According to balanced chemical equation 199 g of A give product mixture = 118 g

 $\therefore 1.99 \text{ g of } A \text{ will give products} = \frac{118 \times 1.99}{199} = 1.18 \text{ g}$ But yield = 1.062 g

So, percentage yield =  $\frac{1.062}{1.18} \times 100 = 90\%$ 

Since, ratio of B and C is 2:1

- $\therefore$  Yield of B = 60% and yield C = 30%
- 4. (c): C removes oxygen from AO and BO but not from MO. So, C is better reducing agent than A and B but not than M. B removes oxygen from AO, B is better reducing agent than A. Better reducing means more active.

Hence, the correct order is M > B > A.

5. (d): Vapour density =  $\frac{\text{Molecular weight}}{2}$ 

As both the compounds have same molecular weights, both will have the same vapour density. Hence, gaseous density of both ethanol and dimethyl ether would be same under identical conditions of temperature and pressure. The rest of these three properties; vapour pressure, boiling point and heat of vaporization will different in isomers of C<sub>2</sub>H<sub>5</sub>OH and CH<sub>3</sub>COCH<sub>3</sub>.

- 6. (c): Equal volume of all gases at STP contain equal number of molecules.
- 7. (c): Since one mole of compound produces three mole of ions, there must be two ions outside the coordination sphere. Since two Cl-atoms are ionizable, the probable formula of the compound is [Co(NH<sub>3</sub>)<sub>5</sub>(NO<sub>2</sub>)]Cl<sub>2</sub>.



#### 8. (d)

9. (a): Acyclic stereoisomers having molecular formula C<sub>4</sub>H<sub>7</sub>Cl can be written as,

Therefore, number of optical isomers =  $2^n = 2^1 = 2$ Two geometrical isomers of each compound are possible for the following structures:

Cl  
10. (c): 
$$2[Ag(CN)_2]_{(aq)}^- + Zn_{(s)} \longrightarrow 2Ag + [Zn(CN)_4]_{(aq)}^{2-}$$

11. (c): In case of nitrogen atom the valence shell cannot have more than 8 electrons because of absence of d-orbitals in it.

12. (b): Let the velocity of particle be x. So, de Broglie wavelength  $(\lambda) = 100x$ 

$$x = \frac{\lambda}{100}$$

$$\lambda = \frac{h}{mv} \Rightarrow \lambda = \frac{h \times 100}{m \times \lambda} \Rightarrow \lambda^2 = 100 \frac{h}{m} \text{ or } \lambda = 10 \sqrt{\frac{h}{m}} \qquad \text{Slope} = \frac{-E_a}{2.303R} = \frac{1}{2.303} \text{ (given)}$$

13. (a): The poisonous element may be As. Thus, we have

AsCl<sub>3</sub> + 6[H] 
$$\xrightarrow{Zn/H_2SO_4}$$
 AsH<sub>3</sub> + 3HCl  
(Soluble) 'N'  
(Poisonous gas)  
2AsH<sub>3</sub>  $\xrightarrow{\Delta}$  2As + 3H<sub>2</sub>↑  
'M'  
(Silver mirror)

Hence M = As and  $N = AsH_3$ .

#### 14. (a)

15. (b): Priority number of atoms bonded to chirality centre is decided on the basis of their atomic number. Higher the atomic number, higher is the priority. Ethynyl or vinyl group has priority over isopropyl group.

#### 16. (c) : Reaction I :

$$H_3C$$
 $CH_3$ 
 $CH_3$ 
 $CHBr_3 + H_3C$ 
 $CHBR_3 + H_3C$ 

Reaction II:

H<sub>3</sub>C CH<sub>3</sub> Br<sub>2</sub> (1.0 mol) H<sub>3</sub>C CH<sub>2</sub>Br + HBr

17. (c): 
$$K_1 = \frac{[C][D]}{[A][B]}; K_2 = \frac{[C]^2[D]^2}{[A]^2[B]^2}$$

therefore 
$$K_2 = K_1^2$$

Since on multiplying equation by any stoichiometric coefficient, electrode potential value does not get multiplied, therefore x = y.

18. (c): 
$$N_2O: \bar{N} = \hat{N} = 0$$

Both N are sp hybridised and are arranged in linear shape.

 $I_3^-: I_3^- (I - I \leftarrow I^-)$  is a trihalide have one covalent and one coordinate bond which involve half filled 5p orbital and vacant 5d orbital respectively. It undergoes sp<sup>3</sup>d hybridization with 2 bp and 3 lp giving trigonal bipyramidal geometry with linear structure.  $N_3^-$ : Central N atom is sp hybridised with 2 bp (terminal N atoms with  $sp^2$  hybridisation) give a linear shape to azide  $(N_3)$  ion.

19. (c): 
$$\log k = \log A - \frac{E_a}{2.303RT}$$

Slope = 
$$\frac{-E_a}{2.303R} = \frac{1}{2.303}$$
 (given)

$$E_a = -2.303 R \times \text{slope} = R = -2 \text{ cal}$$

**20.** (b): As, 
$$K.E. = \frac{3}{2}RT$$

$$\therefore$$
 K.E.  $\propto T$ 

$$\Rightarrow \frac{K.E_{\cdot O_2}}{K.E_{\cdot SO_2}} = \frac{T_{O_2}}{T_{SO_2}} = \frac{273 \text{ K}}{546 \text{ K}} = \frac{1}{2} \Rightarrow K.E_{\cdot SO_2} = 2K.E_{\cdot O_2}$$

$$\therefore K.E._{SO_2} > K.E._{O_2}$$

21. (216.5): 
$$\rho = \frac{Z \times m}{N_A V}$$

$$Z = \frac{\rho N_A a^3}{m} = \frac{2 \times 6 \times 10^{23} \times (5 \times 10^{-8})^3}{75} \approx 2$$

Value of Z represents that the element must have bodycentred cubic structure. For bcc structure, atomic radius

$$=\frac{\sqrt{3}a}{4} = \frac{\sqrt{3}}{4} \times 5 \text{ Å} = 2.165 \text{ Å} = 216.5 \text{ pm}$$

22. (9): Given, 
$$C_V = 2.5 \text{ kJ K}^{-1} = 2500 \text{ J K}^{-1}$$
  
 $\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45 \text{ K}$   
 $\Delta H$  due to combustion of 3.5 g gas =  $C_V \times \Delta T$ 

$$= 2500 \times 0.45 = 1125 \text{ J}$$

Given, molecular weight of gas = 28

$$\therefore$$
 28  $\equiv$  1 mole

Hence,  $\Delta H$  due to combustion of 1 mole of gas

$$=\frac{1125}{3.5}\times28=9000$$
 J

 $\Delta H \text{ in kJ mol}^{-1} = 9000 \text{ J mol}^{-1} \text{ or } 9 \text{ kJ mol}^{-1}$ 

23. (5.14): 
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
  
 $t = 0$  1 0  
 $t_{eqm}$  1 -  $x$  2 $x$ 

Total = 
$$1 - x + 2x = 1 + x$$

As, 
$$PV = nRT = \frac{w}{M}RT$$

$$P = \frac{w}{V} \times \frac{1}{M} RT$$
;  $P = \frac{\rho}{M} RT$ 

$$M = \frac{\rho}{P}RT = \frac{1.84}{1} \times 0.0821 \times 348 = 52.57$$

$$x = \frac{M_{\text{cal}} - M_{\text{obs}}}{M_{\text{obs}}} = \frac{92 - 52.57}{52.57} = 0.750$$

Hence, 
$$K_P = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} = \frac{\begin{pmatrix} 2x \\ 1+x \end{pmatrix}^2}{\begin{pmatrix} 1-x \\ 1+x \end{pmatrix}}$$

f 1 mole of gas  

$$= \frac{1125}{3.5} \times 28 = 9000 \text{ J}$$

$$= \frac{4x^2}{1 - x^2} p = \frac{4(0.750)^2}{1 - (0.750)^2} (1 \text{ atm}) = 5.14 \text{ atm}$$

24. (4): Given:

$$X \longrightarrow Y$$
;  $\Delta_r G^o = -193 \text{ kJ mol}^{-1}$ 

$$M^+ \longrightarrow M^{3+} + 2e^-$$
;  $E^0 = -0.25 \text{ V}$ 

 $F = 96500 \text{ C mol}^{-1}$ 

Let 193 kJ is used for oxidising x moles of  $M^+$ .

For 1 mole of  $M^+$ ,  $\Delta G^{\circ} = -nFE^{\circ}$ 

 $= -2 \times 96500 \times (-0.25) = 48250 \text{ J mol}^{-1} = 48.25 \text{ kJ mol}^{-1}$ 

Thus, no. of moles of  $M^+$  oxidized when one mole of

X is converted to 
$$Y = \frac{193}{48.25} = 4$$

25. (6) : Decapeptide +  $9H_2O \longrightarrow$ 

Glycine + Alanine + Phenylalanine

Total wt. of amino acids after addition of 9 moles of H<sub>2</sub>O

$$= 796 + (9 \times 18) = 958$$

Let *n* units of glycine are present in the decapeptide, then number of glycine unit calculated as,

$$\frac{n \times 75}{958} \times 100 = 47 \implies n = 6$$



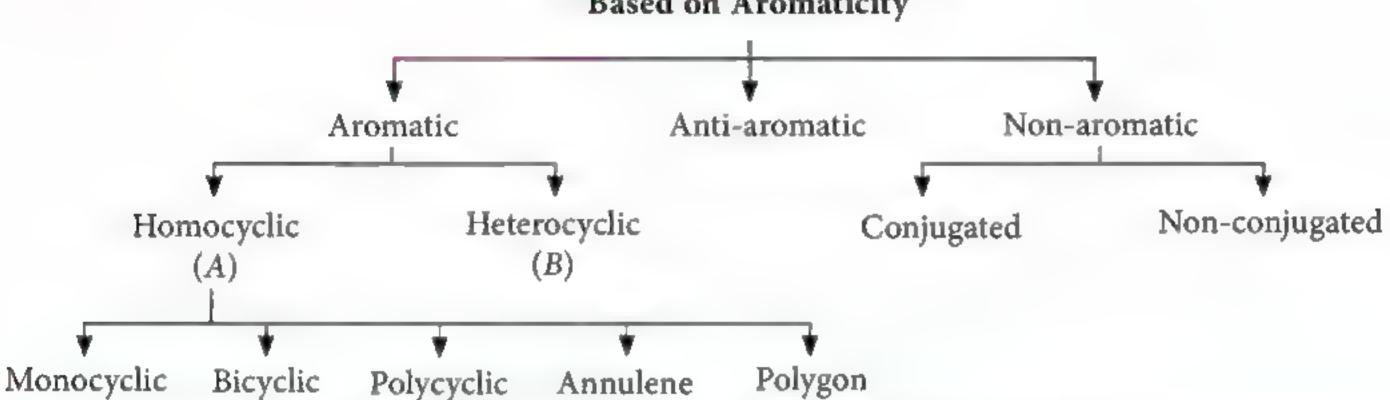


# Rank Enhancer

This column is specially designed to make your concepts crystal clear.

#### AROMATICITY

#### Classification of Compounds Based on Aromaticity



• Comparative study of Aromatic, Anti-aromatic and Non-aromatic compounds:

Aromatic	Anti-aromatic	Non-aromatic	
Cyclic	Cyclic	All compounds which are neither aromatic nor anti-aromatic.	
Conjugated and delocalised over entire ring	Conjugated and delocalised over entire ring		
Planar	Planar		
(4n + 2) number of delocalising electrons	4n number of delocalising electrons		

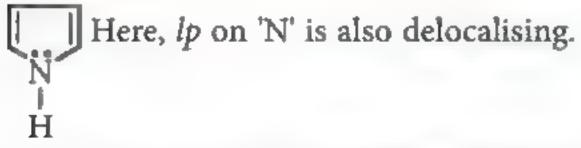
Order of stability: Aromatic > Non-aromatic > Anti-aromatic.

#### CLEAR YOUR MISCONCEPTS

#### **Aromatic Compounds**

1. Delocalising electrons may not be always  $\pi$  electrons. They can be lone pair of electrons.

#### Example:

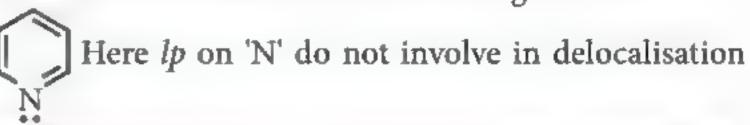


- .. Total number of delocalising electrons
  - =  $2 \times (2\pi \text{ bonds}) + 2 (1 \text{ lp on N})$ =  $2 \times (2) + 2(1) = 6e^{-}$
- 2. If an atom contains two or more *lp* count only one *lp*, delocalising electrons.

Example: Here, 'S' contains two lp, but only one

lp participated in delocalisation.

- .. Total number of delocalising electrons
  - $= 2 \times (2\pi \text{ bond}) + 2 (1 \text{ lp})$
  - $= (2 \times 2) + (2 \times 1) = 6e^{-}$ Sometimes lone pair may not b
- 3. Sometimes lone pair may not be involved in delocalisation if it is associated with  $\pi$ -bond. Hence should not be counted in delocalising electrons.

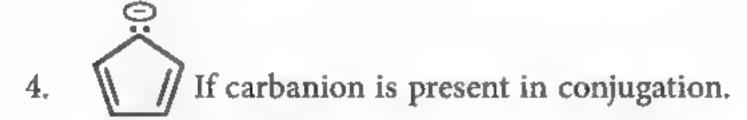


By K. Vijay Bhasker, Senior faculty at Sri Chaitanya Educational Institution, Visakhapatnam

because of presence of  $\pi$  bond on 'N' which is used in delocalisation.

.. Total number of delocalising electrons

$$= 2(3\pi \text{ bonds}) + 0 \times (1 lp) = 6 lp$$



It is considered as planar due to involvement of lp in conjugation, it looses non-planarity character.

Total number of delocalising electrons

= 
$$2(2\pi \text{ bonds}) + 2(1 \text{ lp})$$
  
=  $(2 \times 2) + (2 \times 1) = 6e^{-1}$ 

#### Types of Aromatic Compounds:

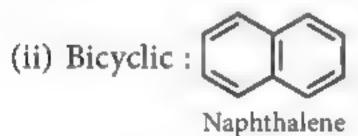
(A) Homocyclic aromatic compounds: Aromatic compounds in which all corners occupied by single type of atoms (i.e., 'C')

#### Example:

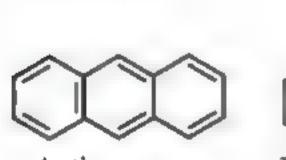


They are further subdivided into five types:

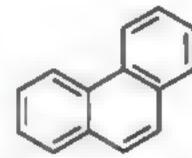




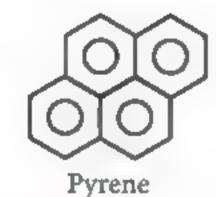
(iii) Polycyclic:



Anthracene

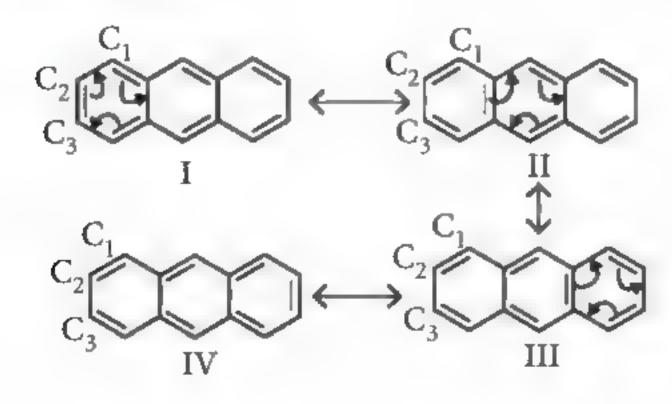


Phenanthrene



#### Special Points for JEE Advanced and AIIMS

(a) In anthracene bond order is not same for all bonds between 'C' atoms.



Bond order of 
$$C_1 - C_2$$
 bond =  $\frac{1+2+2+2}{4} = \frac{7}{4} = 1.75$ 

Bond order of 
$$C_2 - C_3$$
 bond =  $\frac{2+1+1+1}{4} = \frac{5}{4} = 1.25$ 

\*Marked  $\pi$  bond not used in delocalisation. Hence, total number of delocalised electrons =  $7 \times (2\pi e^{-})$ 

$$= 14e^{-}$$

(iv) Annulenes: Completely conjugated monocyclic polyene containing an even number of carbon atoms are called annulene.

Molecular formula =  $C_n H_n$ 

where, n = number of  $\pi$  bonded electrons = number of 'C' atoms



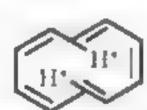
[18] Annulene

Note:



[4] Annulene Anti-aromatic

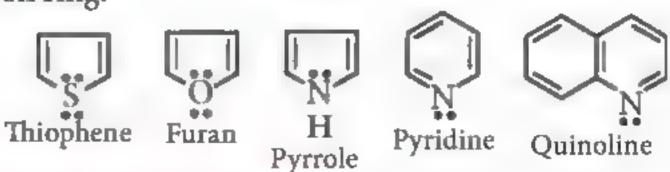
Similarly [12] annulene is also anti-aromatic.



[10] Annulene

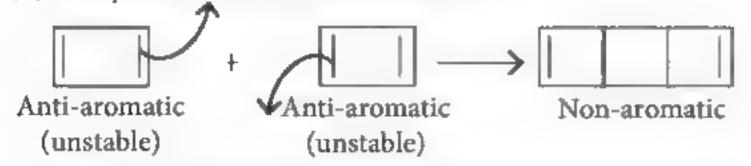
Non-aromatic due to steric hinderance between "H looses planarity.

(B) Heterocyclic aromatic compounds: These are ring compound containing one or more hetero atoms in the carbon ring.

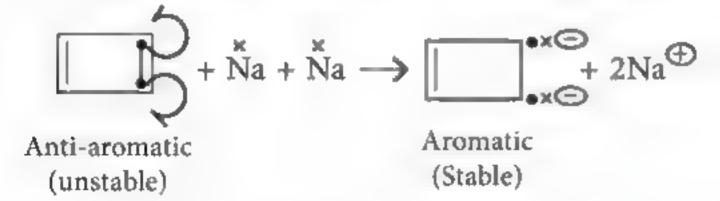


Anti-aromatic compounds: These are most unstable compounds. They get stabilised by any of following 3 methods:

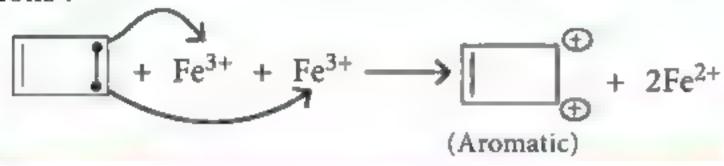
(a) Polymerisation/Dimerisation:



(b) By undergoing reduction on reaction with metals:



(c) By undergoing oxidation on reaction with metal ions:

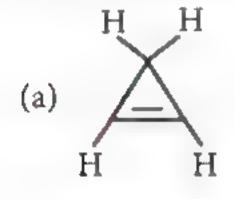


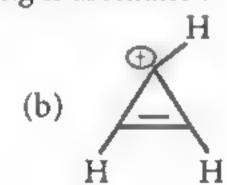
#### **OUESTIONS FOR PRACTICE**

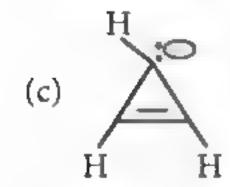
#### **Single Option Correct Type**

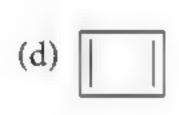


- (a) aromatic
- (b) non-aromatic
- (c) anti-aromatic
- (d) annulene.
- 2. Which of the following is aromatic?

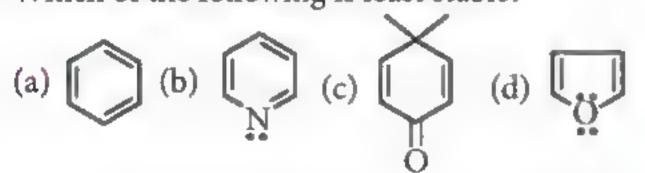








- 3. Number of  $\pi e^-$  in
  - (a) 4
- (b) 8
- (c) 6
- (d) 10
- 4. Which of the following is least stable?

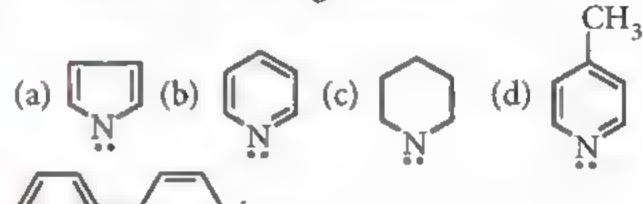


 Azulene have exceptionally high dipole moment due to

- (a) anti-aromaticity
- (b) non-aromaticity
- (c) aromaticity attained by transfer of e-
- (d) high electronegativity difference.
- 6. Pyrene +  $Br_2 \rightarrow Product$

If pyrene is aromatic, it undergoes

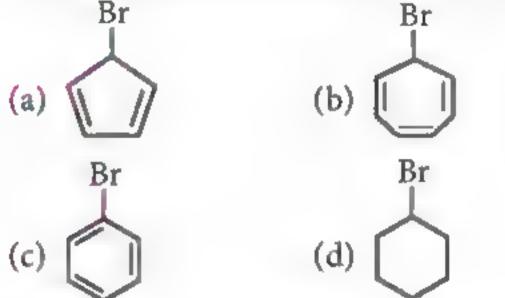
- (a) electrophilic aromatic substitution
- (b) elimination
- (c) condensation reaction
- (d) addition reaction.
- 7. Which of the following is least basic?



8. \_\_\_\_\_ is

anti-aromatic

- (b) non-aromatic
- (c) aromatic
- d) none of these.
- 9. Which of the following react fast with Ag+?



- 10. Which of the following is most acidic?
  - (a) A
  - (b) B

(A)

(B)

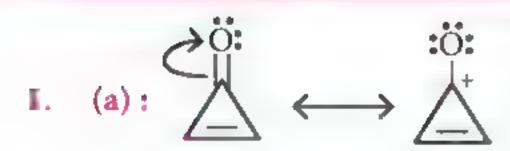
- (c) Both are equally acidic.
- (d) None of these is acidic.

#### **Matching List Type**

11. Match the following:

	~		
(1)	Cyclopentadienyl anion	A.	All 'C' are sp <sup>2</sup> hybridised
(2)	Hexa 1, 3, 5 triene	В.	Compound is anti-aromatic
(3)	Cyclopropene	C.	Complete delocalisation takes place
(4)	Cyclopropenyl anion	D.	Non-aromatic
		E.	Obeys Huckle's rule of aromaticity

#### **Hints & Solutions**

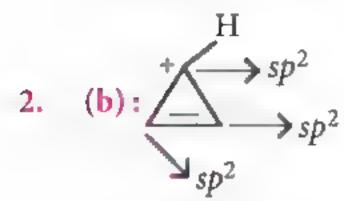


(i) Cyclic

(ii) Planar

(iii) Complete delocalisation

(iv)  $(4n + 2)\pi e^- = 2\pi e^-$ 



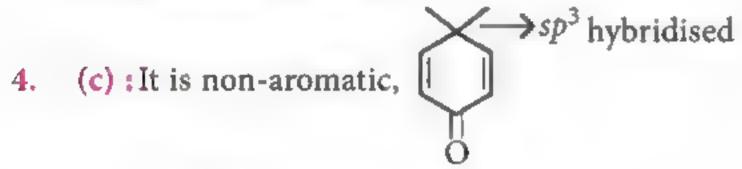
(i) Cyclic

(ii) Planar

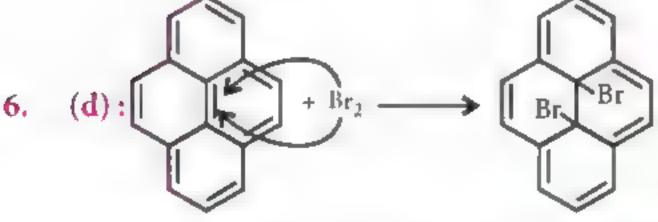
(iii) Complete conjugation

(iv)  $2\pi e^{-}$ 

3. (c) :  $2\pi$  bonds and 1 lp on oxygen involved in delocalisation hence  $6\pi$   $e^-$ 



sp<sup>3</sup> hybridised, non-planar. Rest of all are aromatic.



Central  $\pi$  bond is not involved in delocalisation. It shows addition reaction.

- 7. (a):Lone pair of 'N' is used for aromaticity which further gives stability. Hence, less available for donation.
- 8. (c): In biphenyl even though, total number of  $\pi$  electrons are  $12(4n\pi)$  it maintains aromaticity in each cyclic ring separately.
- (b): Because it becomes aromatic by loosing Brion.

10. (b): 
$$+ \bar{O}H \longrightarrow Anti-aromatic (unstable)$$

H
H
H

Anti-aromatic (unstable)

H

H

Non-aromatic (stable)

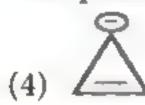
11.  $1 \rightarrow A$ , C, E;  $2 \rightarrow A$ , C, D;  $3 \rightarrow D$ ;  $4 \rightarrow A$ , B, C



All 'C'  $sp^2$  hybridised, conjugation throughout the ring and  $6\pi e^-$  available.

All 'C' sp<sup>2</sup> hybridised, complete conjugation non-cyclic, hence a non-aromatic.

Non-planar, non-conjugation, hence non-aromatic.



All 'C'  $sp^2$  hybridised,  $4\pi e^-$  complete conjugation hence anti-aromatic

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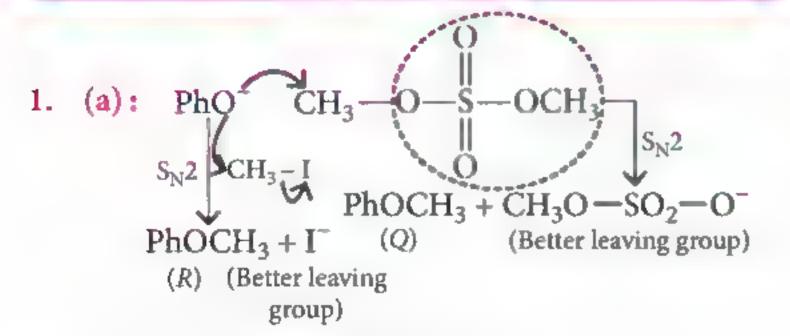
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## CHEMISTRY MUSING

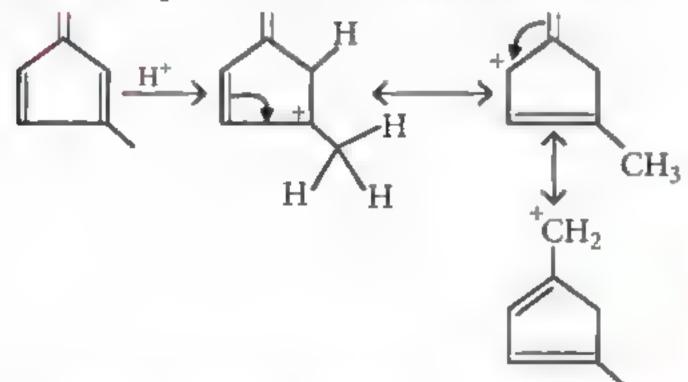
#### **SOLUTION SET 74**



2. (b): [Fe(H<sub>2</sub>O)<sub>5</sub>NO]<sup>2+</sup>
Here, Fe has +1 oxidation state.
Hybridisation: sp<sup>3</sup>d<sup>2</sup> (n = 3), μ<sub>eff</sub>: 3.89 B.M.
Inspite of electronic transition from NO to Fe<sup>2+</sup>, total number of electrons remain same.

Hence, EAN does not change.

3. (a): After protonation carbocation is formed.



Extended resonance makes the carbocation more stable.

4. (a): Let the degree of dissociation in both the reactions be  $\alpha$ .

Initial no. of mol 
$$a$$
  $0$   $b$   $0$   $0$ 

At eqm.  $a(1-\alpha)$   $2a\alpha$   $b(1-\alpha)$   $b\alpha$   $b\alpha$ 

Total no. of moles =  $a(1-\alpha) + 2a\alpha = a(1+\alpha)$ ;  $b(1-\alpha) + b\alpha + b\alpha = b(1+\alpha)$ 

Mole fractions:

$$X_X = \frac{1-\alpha}{1+\alpha}, X_Y = \frac{2\alpha}{1+\alpha}, X_Z = \frac{1-\alpha}{1+\alpha}, X_P = X_Q = \frac{\alpha}{1+\alpha}$$

Partial pressure:

$$p_X = \frac{1 - \alpha}{1 + \alpha} P_1, p_Y = \frac{2\alpha}{1 + \alpha} P_1, p_Z = \frac{1 - \alpha}{1 + \alpha} P_2, p_P = p_Q = \frac{\alpha}{1 + \alpha} P_2$$

Then, 
$$K_{P_1} = \frac{p_Y^2}{p_X} = \frac{\left(\frac{2\alpha}{1+\alpha}P_1\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P_1\right)} = \frac{4\alpha^2 P_1}{1-\alpha^2},$$

$$K_{P_2} = \frac{p_P p_Q}{p_Z} = \frac{\left(\frac{\alpha}{1+\alpha}P_2\right)^2}{\left(\frac{1-\alpha}{1+\alpha}P_2\right)} = \frac{\alpha^2 P_2}{1-\alpha^2}$$

$$\therefore \frac{K_{P_1}}{K_{P_2}} = \frac{\left(\frac{4\alpha^2 P_1}{1-\alpha^2}\right)}{\left(\frac{\alpha^2 P_2}{1-\alpha^2}\right)} = \frac{4P_1}{P_2} = \frac{1}{9} \implies \frac{P_1}{P_2} = \frac{1}{36}$$
(d):

### CHEMISTRY PUZZLE SOLUTION SEPTEMBER 2019

BEAKER	BELL JAR
BOILING TUBE	BOTTLE
BUCHNER FLASK	BUCHNER FUNNEL
BURETTE	CONDENSER
CRUCIBLE	DESSICCATOR
ERLENMEYER BULB	ERLENMEYER FLASK
EUDIOMETER	EVAPORATING DISH
FLORENCE FLASK	FREIDRICH CONDENSER
FUNNEL	GRADUATED CYLINDER
JAR	MICROSCOPE SLIDE
PETRI DISH	PIPETTE
RETORT	SEPARATORY FUNNEL
STIRRING ROD	STOPCOCK
TEST TUBE	THISTLE TUBE
VOLUMETRIC FLASK	WATCH GLASS

6. (b): Packing fraction =  $\frac{\text{Area occupied by circle}}{\text{Area of unit cell}}$ Let edge length = l

Thus, radius 
$$(r) = l/2$$

From figure, it is clear that parallelogram has one complete circle. Thus, area of circle = 
$$\pi r^2 = \pi \left(\frac{l}{2}\right)^2$$

Area of parallelogram = 2 (area of 
$$\Delta ABC$$
)

Area of 
$$\triangle ABC = \frac{1}{2}BC \times AD$$

$$AD^{2} = AB^{2} - BD^{2}$$
$$= l^{2} - \frac{l^{2}}{4} = \frac{3l^{2}}{4}$$

$$\therefore AD = \sqrt{3} \left( \frac{1}{2} \right)$$

$$\therefore \text{ Area of } \Delta ABC = \frac{1}{2} \left( l \times \sqrt{3} \frac{l}{2} \right) = \sqrt{3} \frac{l^2}{4}$$

 $\therefore$  Area of parallelogram = 2 × Area of  $\triangle ABC$ 

$$=2\sqrt{3} \frac{l^2}{4} = \sqrt{3} \frac{l^2}{2}$$

.. Packing fraction = 
$$\frac{\pi l^2 / 4}{\sqrt{3} l^2 / 2} = \frac{\pi}{2\sqrt{3}} = 0.907$$

7. (b): In original mixture only N, N-dimethylaniline forms salt with HCl and that is soluble in NaOH. Amongst remaining, only benzoic acid and p-cresol can form salt with NaOH.

$$H_3C$$
  $O^-Na^+$ ,  $C_6H_5COO^-Na^+$ 

Further only C<sub>6</sub>H<sub>5</sub>COO<sup>-</sup>Na<sup>+</sup> can exist in NaHCO<sub>3</sub> layer (Test to distinguish phenol and carboxylic acid).

- 8. (d): Benzaldehyde forms bisulphite with NaHSO<sub>3</sub>.
- 9. (0.4): CO<sub>2</sub> is reduced to CO when it is passed over red hot coke.

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$$

Since 1 volume of CO<sub>2</sub> produces 2 volume of CO, had all of the CO<sub>2</sub> been converted to CO, the final volume of gas would have been 2 L. However, the final volume is less than 2 L, so some CO<sub>2</sub> must have remained unchanged.

Let x L of CO<sub>2</sub> changed into CO.

Then the volume of the  $CO_2$  left = (1 - x) L

And the volume of CO produced = 2x L

The total volume of gas = (1 - x) L + 2x L = (1 + x) L(1 + x) L = 1.6 L

$$\therefore x = 0.6$$

Thus, the composition of the gaseous mixture:

$$CO_2 = (1 - 0.6) L = 0.4 L$$
,  $CO = 2 \times 0.6 L = 1.2 L$ 

10. (89.24): 
$$A = \frac{k_1}{k_2}$$

At 
$$t = 0$$
 2 mol litre<sup>-1</sup> 0  
At eq.  $(2 - X)$  mol litre<sup>-1</sup> X

$$k_1 = 2 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1} \text{ (zero order)}$$

$$k_2 = 3 \times 10^{-3} \text{ s}^{-1} \text{ (1st order)}$$

$$\frac{dX}{dt} = k_1 [A]^0 - k_2 [B]^1$$

At equilibrium, 
$$\frac{dX}{dt} = 0$$
  $\therefore$   $0 = k_1 - k_2[X]_{eq}$ .

$$\therefore [X]_{eq.} = \frac{k_1}{k_2} = \frac{2 \times 10^{-3}}{3 \times 10^{-3}} = 0.66 \text{ mol litre}^{-1}$$

$$A \iff B$$
At initial eq. 1.34 0.66

At initial eq. 1.34 0.66  
At eq. Moles added 1.34 
$$0.66 + 0.5 = 1.16$$

At time 
$$t$$
 (1.34 +  $X$ ) (1.16 -  $X$ )

Addition of *B* will bring backward reaction at time *t*.

$$B = \frac{3}{4}[A]_{eq} = \frac{3}{4} \times 1.34 = 1.005$$

$$(1.16 - X) = 1.005$$
  $\therefore X = 0.155$ 

Now, 
$$\frac{dX}{dt} = k_1 - k_2[X] = 0.66 k_2 - k_2 X = k_2(0.66 - X)$$

$$\therefore \frac{dX}{(0.66-X)} = k_2 \cdot dt$$

or 
$$-2.303 \log (0.66 - X) = k_2 \cdot t + C$$

At 
$$t = 0$$
,  $X = 0$  :.  $C = -2.303 \log 0.66$ 

$$k_2 \cdot t = 2.303 \log \frac{0.66}{0.66 - X}$$

$$t = \frac{2.303}{3 \times 10^{-3}} \log \frac{0.66}{0.66 - 0.155} = 89.24 \text{ s}$$

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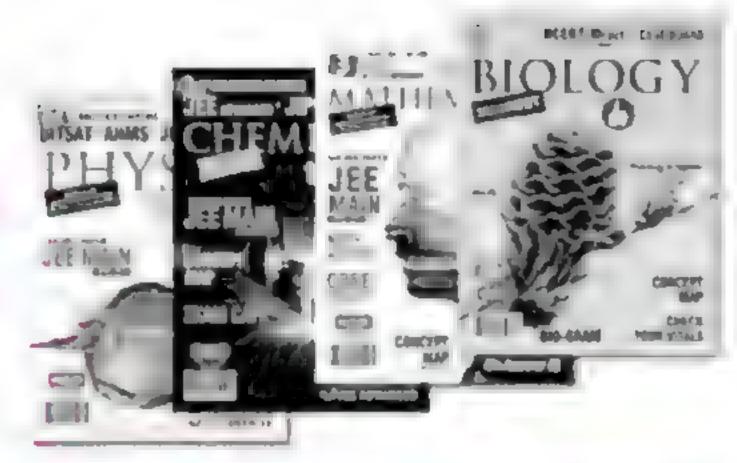
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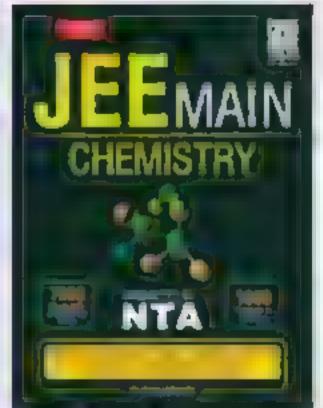
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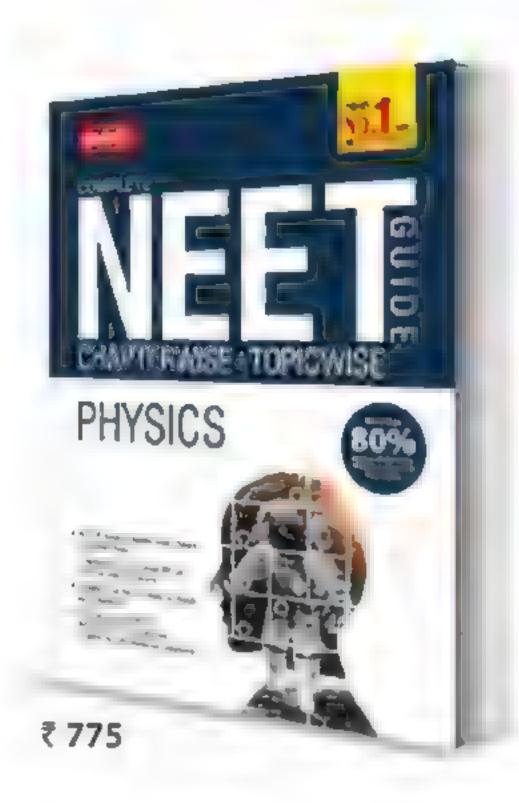


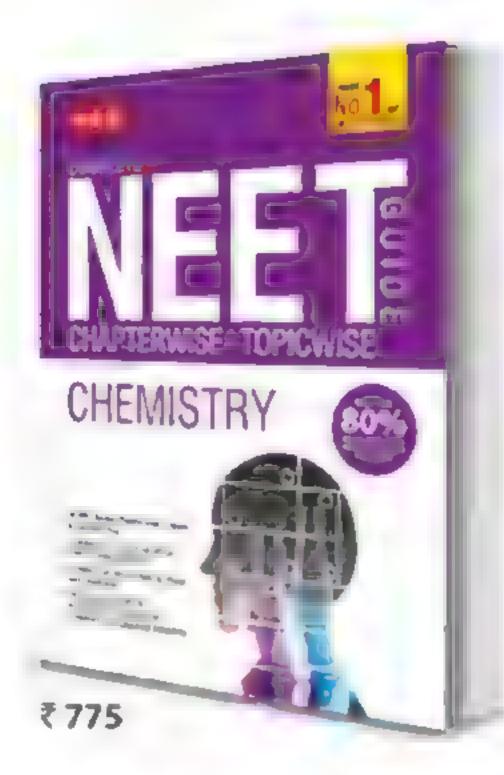
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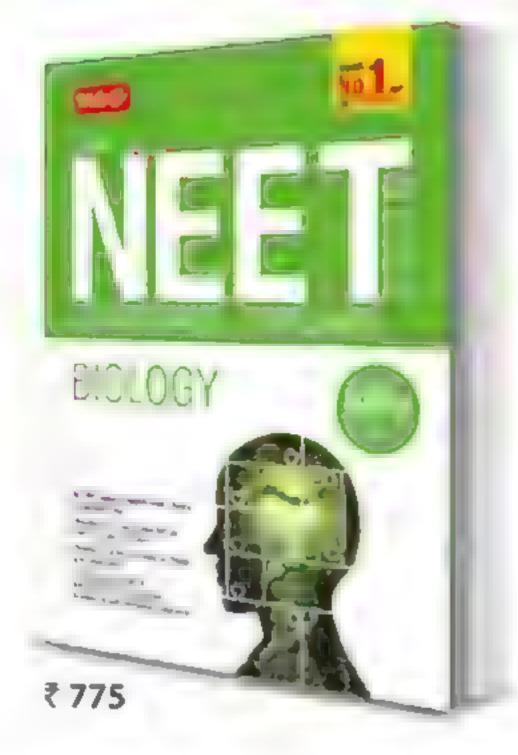
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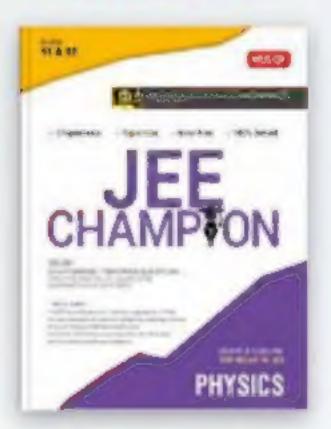


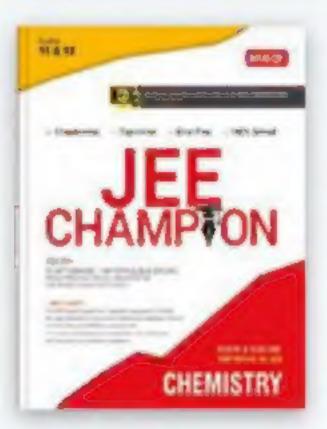


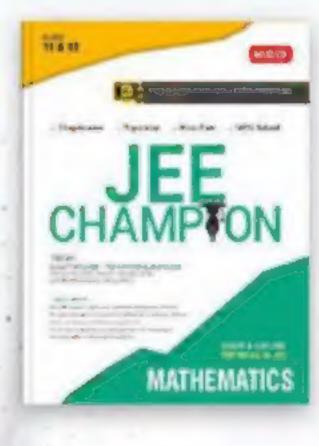
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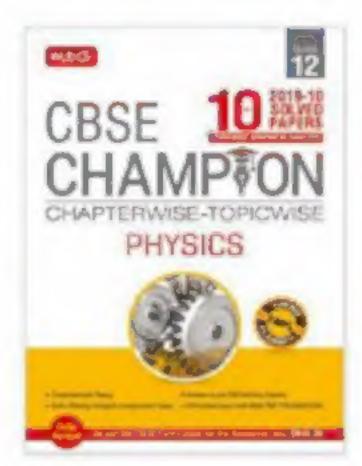
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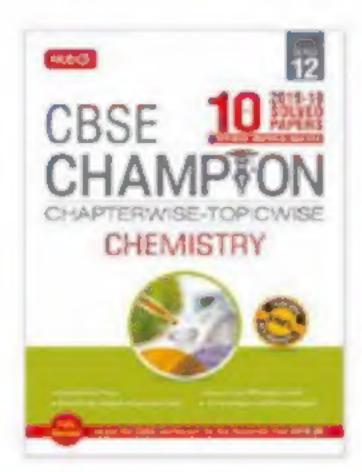


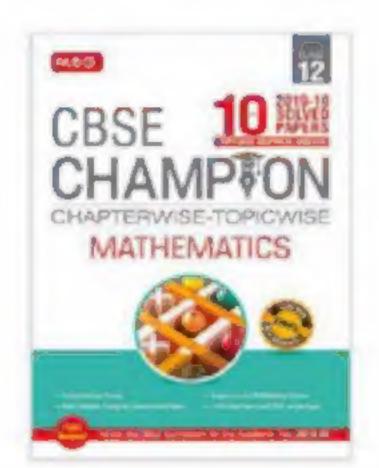
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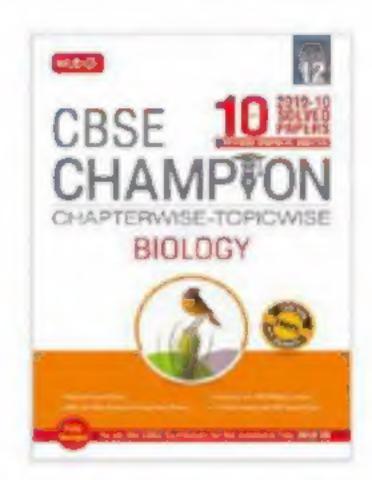


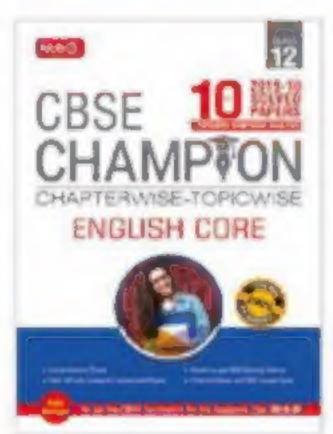
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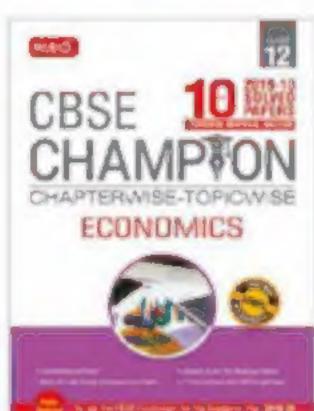




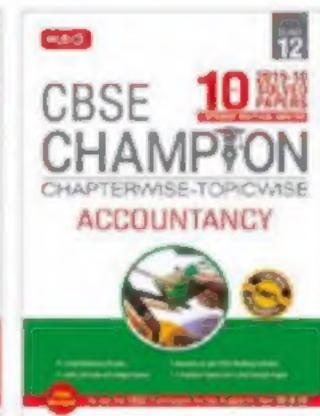


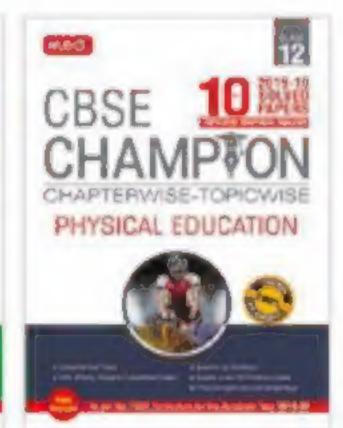


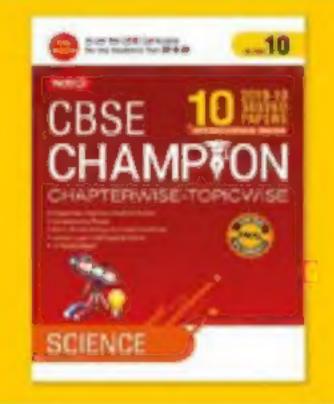


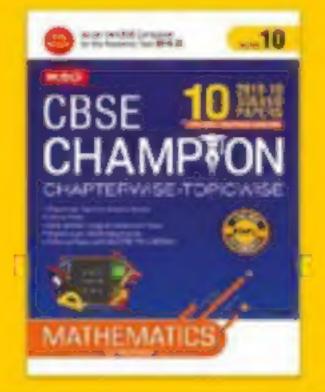


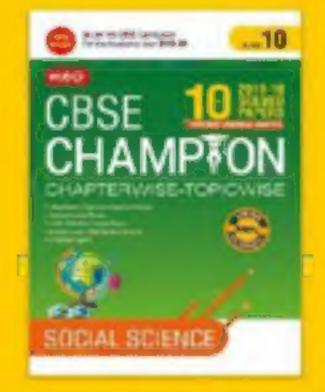


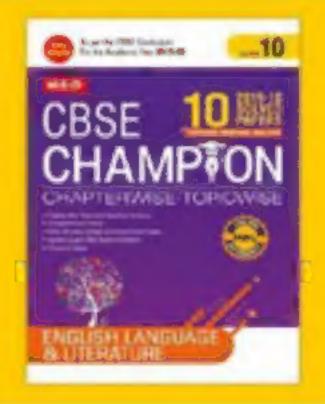


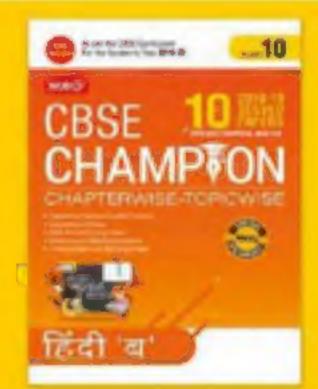












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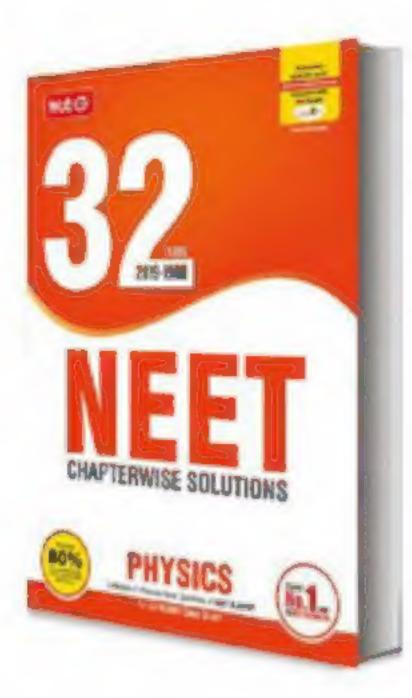


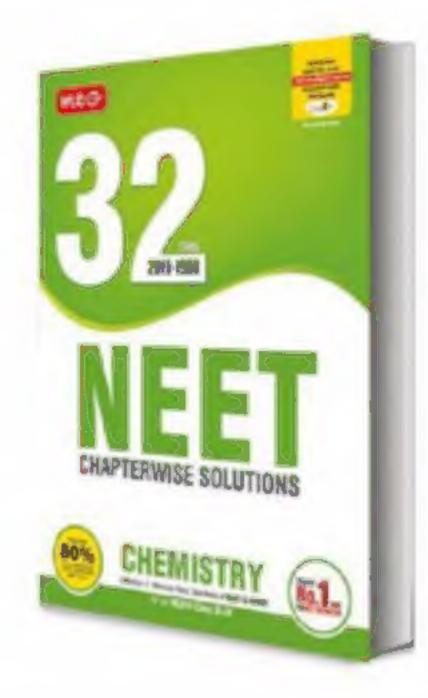


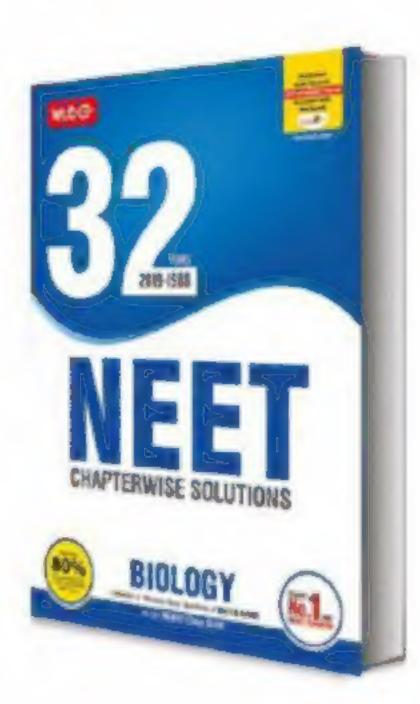
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#### HIGHLIGHTS:

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